

Oxidation of Hydrocarbons in the (Cont.)

SOV/3663

Knorre, D.G., L.G. Chuchukina, and N.M. Emanuel' [Institute of Chemical Physics]. Dual Function of Metal Stearates in the Hydrocarbon Oxidation Reaction

145

The dual role of copper and manganese stearates as both catalysts and inhibitors of oxidation of iso- and n-decane is described. The authors determine the critical concentration of cupric stearate ($\sim 0.03\%$ per mole) above which the induction period for n-decane oxidation increases.

Mayzus, Z.K., L.G. Privalova, and N.M. Emanuel' [Institute of Chemical Physics]. Change in the Mechanism of n-Decane Oxidation in the Course of the Reaction

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The authors have used C^{14} tagged n-decane to investigate changes in the rates of formation and consumption of n-decyl hydroperoxides during the oxidation of n-decane. The hypothesis that variations in the activities of radicals carrying on chain reactions are proportional to the accumulation of oxygen-containing oxidation products in the reacting mixture is offered as a possible explanation of the phenomenon.

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5(4)

AUTHORS:

Babayeva, A. A., Mayzus, Z. K.,
Emanuel', N. M.

SOV/62-59-8-6/42

TITLE:

Oxidation Kinetics of Isobutane in the Presence of
Hydrogen ~~Bromide~~

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 8, pp 1378-1385 (USSR)

ABSTRACT:

In the present paper the investigation of the catalytic oxidation of hydrocarbons is continued and the oxidation kinetics of ramified hydrocarbons (in this case isobutane in the presence of HBr) is investigated by means of HBr. This reaction is very sensitive to the surface condition of the reaction vessels. Thus molybdene-glass vessels covered with a layer of boron oxides were used. The oxidation was carried out on a vacuum unit under static conditions. A figure shows the unit used. The way in which the reaction products were removed from the vessels is described. The peroxides obtained in the reaction were identified polarographically (peroxides of tertiary butyl, tertiary butyl alcohol, and acetone). Very definite stages were observed in the reaction process. In the first stage isobutane is mainly oxidized so that it forms the

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Oxidation Kinetics of Isobutane in the Presence of
Hydrogen Bromide

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hydroperoxide of tertiary butyl; in the second stage the oxygen consumption drops and the reaction takes place via the formation of the hydroperoxide of butyl alcohol and the decomposition of the peroxide while acetone is formed. These facts were obtained by means of the determination of the yields under varying reaction conditions (changes in the concentration of initial materials) (Figs 3,4). The summary reaction process is represented by the following equations:
$$i-C_4H_{10} + O_2 \rightarrow (CH_3)_3COOH, (CH_3)_3COOH + (CH_3)_3CH \rightarrow (CH_3)_3COH + (CH_3)_2CO + CH_4.$$
 There are 5 figures, 4 tables, and 14 references, 9 of which are Soviet.

ASSOCIATION:

Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences, USSR)
Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova
(Moscow State University imeni M. V. Lomonosov)

SUBMITTED:
Card 2/2

December 27, 1957

BABAYEVA, A.A.; MAYZUS, Z.K.; EMANUEL', N.M.

Changes in the chemistry of the oxidation of isobutane in the presence of HBr as affected by additions of reaction end products. Dokl.AN Azerb.SSR 15 no.11:1009-1013 '59.
(MIRA 13:4)

1. Kafedra khimicheskoy kinetiki Moskovskogo gosudarstvennogo universiteta imeni Lomonosova i Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom AN Azerbaydzhanskoj SSR M.F. Nagiyevym.

(Propane) (Oxidation)

5(4)

AUTHORS:

Knorre, D. G., ~~Mayzua, Z. K.~~
Markin, M. I., Emanuel, N. M.

SOV/76-33-1-36/45

TITLE:

The Kinetics of the Valence Changes of Manganese Stearate in the Course of the Initial Macroscopic Stage of the Catalytic Oxidation of n-Decane (Kinetika valentnykh prevrashcheniy stearata margantsa v khode nachal'noy makroskopicheskoy stadii katalizirovannogo okisleniya n-dekana)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 1, pp 213-218 (USSR)

ABSTRACT:

A short time ago it was found (Refs 1-3) that on the oxidation of n-decane (I) several changes take place in the laurates and stearates of manganese and cobalt. A valence change of the catalyzer takes place which causes its falling out and becoming ineffective (Ref 4). In the case under discussion the kinetics of the accumulation of colored intermediate products of these catalyzers are investigated. The oxidation of (I) took place in a way already described. The samples were examined in the wave length of 400 m μ by the spectrophotometer SF-4. It is stated that the effective activation energy of the accumulation of the intermediate products of manganese stearate is 8.1 kcal on the

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The Kinetics of the Valence Changes of Manganese Stearate in the Course of the Initial Macroscopic Stage of the Catalytic Oxidation of n-Decane SOV/76-33-1-36/45

oxidation of (I), whereas the activation energy of the further reduction of the intermediate compound is 16.1 kcal. The absorption coefficients of the intermediate compound were determined in cumene (since it is simpler than in (I)) and at 400 m μ the value 780 l/g-mol cm was found. Beer's (Ber) law is followed up to a catalyzer concentration of 0.016 m (Fig 7). Tests with (I), tetralin, and cumene showed that the absorption coefficient of the intermediate compound obviously does not depend too much on the hydrocarbon to be oxidized (Fig 6). The kinetic curves of the accumulation of colored intermediate products show an initial acceleration (Fig 7). At the curve maximum cumene and tetralin show a complete transition of manganese stearate to a higher valence stage and (I) a 30.5% transition only. There are 8 figures and 4 Soviet references.

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

SUBMITTED: July 17, 1957

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5(4)

SOV, 76-33-0-0114

AUTHORS:

Khorre, D. G., Nayzov, Z. K., Markin, M. I., Emanuel', N. M.

TITLE:

Kinetics of the Reaction Between Decyl Hydroperoxide and Manganous Stearate in n-Decane (Kinetika vzaimodeystviya gidroperekhisi deitsila so stearatom manganitsa v n-dekane)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, No 2, pp 398 - 404 (USSR)

ABSTRACT:

Several papers on the oxidation kinetics of hydrocarbons involving manganese or cobalt catalytic report that the catalyst is observed to assume a higher valence number. In regard to this several hypotheses have been put forth by Ye. T. Derisov and N. M. Emanuel' (Ref 6), P. V. Korotkiy and L. I. Shirko (Ref 7), and others (Refs 4,5). The question of through what reaction the change in the valence of the catalyst takes place has until now, however, not been explained. The first experiments carried out in the work reported in this paper showed that the reaction mentioned in the title occurs very fast. It was for this reason that an apparatus was constructed (Fig 1) which could directly measure the optical density of the reaction medium. The

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Kinetics of the Reaction Between Danyl Hydroperoxide
and Manganese Stearate in n-Decane

SOV/76-11-100/41

apparatus is similar in principle to the SF-4 spectrophotometer. The kinetic curves obtained with various concentrations of the manganese stearate (I) show (Fig. 2) that the reaction is complex. The reaction is a first order reaction (Figs 3, 5). The kinetic curves (Fig. 4) for 35°C show that a maximum transformation occurs with ratios of (I): danyl hydroperoxide (II) of 0.7-0.9, at 4.83-5.6%, and 7.23-10%. An increase in temperature increases the velocity of the oxidation reaction as well as its depth, whereby there is also a decrease in the induced decomposition of (II), which occurs in addition to the accumulation of the oxidized form of (I). Since the rate of the induced decomposition of (II) is unknown only the upper limit of the activation energy could be reliably determined (20.5 kcal), but for a first approximation of the activation energy a value of 16 kcal was obtained. The rate constant for the reaction giving an accumulation of the colored reaction product (oxidized form of (I)) is written as

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$k = 2.8 \cdot 10^{11} e^{-10000/RT}$ 1/mole.sec. There are 7 figures

Kinetics of the Reaction Between Decyl Hydroperoxide
and Manganous Stearate in n-Decane

SOV/76-37-2-3,745

12 references, 5 of which are Soviet.

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

SUBMITTED: July 17, 1957

Card 3,3

5(4)

AUTHORS:

Denisov, Ye. T., Mayzus, Z. K. ~~SOV/20-128-4-33/65~~
Skibida, I. P., Emanuel, N. M., Corresponding Member, AS USSR

TITLE:

Kinetic Laws for Autocatalytic Reactions in Open Systems

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 4,
pp 755-758 (USSR)

ABSTRACT:

In chemical technology, the continuous process of reactions is attempted more and more, i.e. of reactions in open systems. While the kinetics of simple processes had already been investigated (Refs 2-4), no data are available on autocatalytic processes. Therefore, the continuous oxidation of cyclohexanone to adipic acid by oxygen at 130° was studied. The apparatus used permitted the automatic maintenance of the inflow of raw material and of the outflow of the reaction products. The term of "specific velocity" v is defined as the volume of the liquid initial component supplied to the unit of volume of the reaction vessel in the unit of time.

The value $\frac{1}{v}$ indicates the average duration of stay of the liquid in the reaction vessel. The content of hydrogen peroxide, adipic acid, and CO₂ in the reaction product is

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determined for different v . In the continuous process, a stationary state appears, i.e. the reaction rate and the discharge of the end product are in an equilibrium relation to each other. Figure 1 shows the dependence of the equilibrium concentration of adipic acid on v . In the transition from the periodic process to the continuous one, it is of no importance in which phase of reaction this transition takes place since the equilibrium concentration is formed corresponding to v , irrespective of the oxidation degree attained. While for simple reactions the rate rises monotonously with v , there is a different dependence for autocatalytic reactions since not only the concentration of the initial product but also that of the resulting intermediate product (hydrogen peroxide) is decisive. Figure 3 shows that the reaction rate passes a maximum at a certain v ; if v keeps on rising, the reaction rate falls since the concentration of the hydrogen peroxide becomes lower. The equation for the maximum reaction rate is written down. It is pointed out that in the continuous process, in comparison with the periodic process, a smaller amount of burning to CO_2 and H_2O

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Kinetic Laws for Autocatalytic Reactions in
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occurs because the reaction products remain in the
reaction zone for a shorter period. There are 3 figures
and 6 references, 3 of which are Soviet.

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

SUBMITTED: June 22, 1959

Card 3/3

85604

S/062/60/000/006/023/025/XX
B020/B060

11.1210 also 2209

AUTHORS: Babayeva, A. A., Mayzus, Z. K., and Emanuel', N. M.

TITLE: Part Played by the Surface in the Macroscopic Stages of
Isobutane Oxidation Reaction in the Presence of HBr

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk.
1960, No. 6, pp. 976-980

TEXT: The oxidation mentioned in the title consists of two distinct macroscopic stages separated in time (oxidation of isobutane with oxygen on tert. butyl hydroperoxide, and decomposition of hydroperoxide and its reaction with the initial hydrocarbon). The differential-calorimetric method suggested by A. A. Koval'skiy (Ref. 5) was used for the study of the oxidation kinetics, and further evidence was found for the two-stage reaction course, and the part played by the surface in the macroscopic stages of this reaction was defined. The reaction was studied in a static vacuum system. A Mo-glass reaction vessel was washed out with a boric acid solution for surface stabilization (Ref. 6). The differential thermocouple

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Macroscopic Stages of Isobutane Oxidation
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B020/B060

consisted of a constantan wire and several copper wires entered into 0.44-mm quartz capillaries. The junction for the measurement of temperature in the central zone was fixed in the central capillary, and the junction for the measurement of the wall temperature was fixed on the vessel wall. The heat flow between the temperature in the center of the reaction mixture and on the vessel wall was measured by a mirror galvanometer with an accuracy of $2.8 \cdot 10^{-9}$ a/mm/m. The kinetic curves of the accumulation of tert. butyl hydroperoxide and the heating curves of the reaction mixture during the isobutane oxidation in the presence of HBr are shown in Fig. 1, while the temperature dependence of ΔT_{\max} (heating maximum) is illustrated in Fig. 2. The activation energy determined from the inclination of the straight line is 16.8 kcal/mole, which is in good agreement with the value of 16.4 kcal/mole found earlier from the kinetic curves of the accumulation of tert. butyl hydroperoxide. Tests made by applying a KCl layer first onto the reaction surface vessel and then onto the surface of the central capillary revealed that the heating of the reaction mixture, which corresponds to the reaction rate in the hydroperoxide formation, is

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Part Played by the Surface in the
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S/062/60/000/006/023/025/XX
B020/B060

caused by the liberation of heat in the reaction vessel interior and not on its surface. For a proof of the heterogeneity of the second reaction stage, the reaction vessel was filled with packing material. The kinetic curves of the hydroperoxide accumulation with packing material in the vessel (Fig. 3) distinctly showing the different effects of the packing material upon the first and the second reaction stage. The effect of the packing material is the same at 150° and 170°C. The missing effect of the packing material upon the kinetics of the process in the first stage proves the homogeneous character of the tert. butyl hydroxide formation with a heterogeneous initiation of the chains. The rate increase in the second reaction stage with enlarged vessel surface proves the heterogeneous character of this stage. In the oxidation of isobutane in the presence of HBr there occurs partly a decomposition of tert. butyl hydroperoxide under formation of acetone, and partly its reaction with isobutane to form tert. butyl alcohol. In the presence of packing material (Fig. 4) the amount of resulting acetone is increased, and that of tert. butyl alcohol is decreased. There are 4 figures and 6 references: 5 Soviet and 1 US.

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Part Played by the Surface in the
Macroscopic Stages of Isobutane Oxidation
Reaction in the Presence of HBr

S/062/60/000/006/023/025/XX
B020/B060

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

SUBMITTED: December 16, 1958

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Card 4/4

82654

S/195/60/001/001/003/007
B015/B060

5.3200

AUTHORS: Mayzus, Z. K., Skibida, I. P., Emanuel', H. M.
Yakovleva, V. N.

TITLE: Chain- and Molecular Reactions of Intermediates in the
Oxidation of n-Decane

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 1, pp 55-62

TEXT: The authors studied the decomposition kinetics of the hydroperoxides of n-decyl in n-decane in the presence of α -naphthene acting as an inhibitor. The latter was added at various stages of the reaction. The constant of hydroperoxide decomposition without chain reaction was calculated from the kinetic curves and was found to equal $1.7 \cdot 10^{-3} \text{ min.}^{-1}$. It is near the value of the reaction rate constant of the reaction chain branching in the oxidation of n-decane ($k = 1.1 \cdot 10^{-3} \text{ min.}^{-1}$). From this the authors concluded that, besides the decomposition of the hydroperoxide molecules into radicals without chain reaction, there also takes place a molecular decomposition under the formation of ketones and water. α -naphthene was found to react not only,

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in the Oxidation of n-Decane

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B015/B060

with the RO_2 radical but also with RO radicals developing in the hydroperoxide decomposition. The formation of free radicals with the chain branching occurs in parallel to two reactions: the monomolecular decomposition of the hydroperoxide $ROOH \rightarrow RO + OH$ and the reaction of the hydroperoxide with the hydrocarbon $ROOH + RH \rightarrow RO + H_2O$. The authors established the effective reaction rate constant of the chain branching reaction in the oxidation of n-decane as the sum of the constants of the monomolecular decomposition of the hydroperoxide (in chlorobenzene as an inert solvent) and of the bimolecular reaction of the hydroperoxide with n-decane. The reaction rate constant of the bimolecular branching reaction rises with the weakening of the C-H bond in the hydrocarbon in the following order: decane < isodecane < ethyl benzene < methyl oleate. In the oxidation of n-decane, the alcohols were found to be formed by a chain reaction and (partly) a molecular reaction, while they are used up only by a chain reaction. The ketones are formed by a chain reaction, and are likewise used up by a chain reaction. N. N. Semenov is mentioned in the text. There are 6 figures and 7 references: 5 Soviet, 1 US, and 1 British.

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82654

Chain- and Molecular Reactions of Intermediates
in the Oxidation of n-Decane

S/195/60/001/001/005/007
B015/B060

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

SUBMITTED: January 4, 1960

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5.4300

88359

S/195/60/001/004/004/015
B017/B055

AUTHORS: Blyumberg, E. A., Zaikov, G. Ye., Mayzus, Z. K., Emanuel',
N. M.

TITLE: Oxidation of Ethyl Alcohol in the Liquid- and the Gaseous
Phase Under Comparable Conditions

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 4, pp. 510-518

TEXT: The kinetics of ethyl alcohol oxidation in the liquid- and the
gaseous phase were investigated at various temperatures and pressures.
Oxidation of ethyl alcohol in the liquid phase was carried out at
145-230°C and 52-95 atm. The kinetic curves representing the ethyl
alcohol consumption and the enrichment of the reaction-product during
liquid-phase oxidation at 52 atm and 145, 200, and 230°C appear in Fig. 1.
The reaction rate increases with temperature. The activation energy of
ethyl alcohol oxidation in the liquid phase is 10.2 kcal/mole. The
reaction products of ethyl alcohol oxidation in the liquid phase at
200°C and 52 atm are tabulated. The main reaction products of oxidation
in the liquid phase are acetic acid and ethyl acetate. Fig. 2 shows the

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Oxidation of Ethyl Alcohol in the Liquid- and
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B017/B055

kinetic curves of ethyl alcohol consumption and enrichment of reaction products during oxydation at 230°C and 52, 70, and 95 atm. The corresponding curves for oxidation in the liquid phase at 52 atm and 145 and 200°C over cobalt acetate are shown in Fig. 3. Both the reaction kinetics and the composition of the reaction products in gaseous phase oxidation of ethyl alcohol differ from those in liquid phase oxidation. In gaseous phase oxidation, CO and acetaldehyde are the main reaction products. The kinetic curves of ethyl alcohol consumption and the enrichment of the reaction product during gaseous phase oxidation (200°C, 20 atm) at ethyl alcohol concentrations of $2.6 \cdot 10^{-3}$ and $0.54 \cdot 10^{-3}$ mole/cm³ are represented in Fig. 4. Fig. 5 shows the corresponding curves for temperatures of 200, 230, 250, and 280°C and 20 atm at alcohol concentrations of $2.6 \cdot 10^{-3}$ mole/cm³. The influence of temperature on the gaseous phase oxidation of ethyl alcohol at 200 and 280°C and 200 atm is illustrated in Fig. 5. The CO and CH₄ contents of the reaction products increase with temperature. The activation energy for the oxidation of ethyl alcohol in the gaseous phase is 18 kcal/mole. N. N. Semenov is mentioned. There are 5 figures, 1 table, and 21 references: 7 Soviet, 8 British,

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Oxidation of Ethyl Alcohol in the Liquid- and
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3 US, 1 Italian, 1 Indian, and 1 Swiss.

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

SUBMITTED: June 10, 1960

Card 3/3

5.3200

AUTHORS:

Mayzus, Z. K., Emanuel', N. M.,
Corresponding Member AS USSR,
Yakovleva, V. N.

68994

S/020/60/131/02/040/071
B004/B007 -

TITLE:

The Mechanism of the Decomposition of Intermediate Hydroperoxides
in the Oxidation of n-Decanes in the Liquid Phase

PERIODICAL:

Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 2, pp 351 - 353
(USSR)

ABSTRACT:

It was the aim of the present paper to determine the quantitative relationship between the molecular and chain-reaction decay of the hydroperoxides of n-decyl in the oxidation of n-decane in an oxygen current at 130°. The investigation was carried out by adding α -naphthol as inhibitor of the decomposition of hydroperoxides in various stages of oxidation. Figure 1 shows the action of α -naphthol upon the concentration of the hydroperoxides. The increase in the concentration of the hydroperoxides is rapidly stopped, in which case, however, the concentration does not remain constant, but a noticeable decomposition of the hydroperoxides by reactions different from chain reactions may be observed. The velocity constant of this reaction is independent of hydroperoxide concentration and equals $1.7 \cdot 10^{-3} \text{ min}^{-1}$. As this value

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The Mechanism of the Decomposition of Intermediate Hydroperoxides in the Oxidation of n-Decanes in the Liquid Phase

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is considerably lower than the constant of the total hydroperoxide decomposition measured in reference 1, the oxygen supply was stopped at a certain concentration of the hydroperoxides, and the decomposition of the hydroperoxides was investigated with and without addition of the inhibitor in nitrogen atmosphere. As shown by the kinetic curves represented in figure 2, the decomposition of the hydroperoxides is considerably inhibited by the inhibitor. The non-chain reaction-like decomposition in the presence of the inhibitor is not influenced by oxygen. As no RO₂-ra-

dicals occur in nitrogen atmosphere, the α -naphthol must enter into reaction with other free radicals; e.g. with RO-radicals. The ratio between the decomposition rate of hydroperoxides by chain- and non-chain reaction does not remain constant in the course of oxidation. The ratio between the decomposition rate in the non-inhibited process and that in the presence of α -naphthol at the same hydroperoxide concentration served the purpose of a qualitative evaluation. The length of the decomposition chain determined in this manner changed from 20 links at the beginning of the reaction (hydroperoxide concentration = 0.6%)

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to 3 links with a hydroperoxide concentration of 2.1%. Figure 3 shows that the decomposition velocity constant rapidly decreases with increasing concentration of α -naphthol to a constant value, which amounts to $1.7 - 1.9 \cdot 10^{-3} \text{ min}^{-1}$. In the course of special experiments, the authors found that no ketones are formed. Measurement of the alcohol concentration and of the hydroperoxide concentration of n-decyl in the presence of phenol as inhibitor resulted in full agreement of these values. This means that the total quantity of alcohol has formed from the hydroperoxides by the transformation of RO-radicals. There are 3 figures and 8 references, 4 of which are Soviet.

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

SUBMITTED: December 14, 1959

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5.3300

69511

AUTHORS:

Mayzus, Z. K., Skibida, I. P.,
Emanuel', N. M., Corresponding Member
AS USSR

S/020/60/131/04/045/073
B004/B125

TITLE:

The Mechanism of Chain Branching in the Reaction of the Oxidation
of n-Decane ¶ 7

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 131, Nr 4, pp 880 - 882 (USSR)

TEXT: The authors discuss the reaction equations $ROOH \rightarrow RO^\bullet + OH^\bullet$ (1),
 $2ROOH \rightarrow RO_2^\bullet + RO^\bullet + H_2O$ (2), and $ROOH + RH \rightarrow R^\bullet + RO^\bullet + H_2O$ (3) in view of
their energetic probability. Their experimental investigations are based on the
fact that the equations (1) and (3) differ from each other by the effective par-
ticipation of the hydrocarbon in equation (3). If equation (3) is valid, then a
dependence of the decomposition of the ROOH compounds (hydrogen peroxides) on the
concentration of the hydrocarbon should be observable. They measured the rate of
the branching of the reaction in solutions of n-decyl hydrogen peroxide in
chlorobenzene and in mixtures of chlorobenzene and n-decane. The hydrogen per-
oxides were obtained by oxidation of the n-decane, converted into sodium salts,
and extracted from the liquid phase by means of chlorobenzene. The rate of the
reaction was determined according to reference 2 on the basis of the consumption

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of the Oxidation of n-Decane

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B004/B125

of the α -naphthol used as an inhibitor. The authors describe the measurement of the concentration of the α -naphthol: double extraction by means of 1 N NaOH, reaction with phenyldiazonium and measuring the intensity of the coloration of the resulting azo-compound by means of an SF-4 spectrophotometer at 520 m μ . They attained the result that the hydrogen peroxides also decompose in pure chlorobenzene and, to be sure, according to equation (1). In the presence of n-decane the rate of decomposition corresponding to equation (3) increases linearly with the increasing concentration of the n-decane (Fig 1). The reaction thus takes place simultaneously monomolecularly as well as bimolecularly. For the monomolecular reaction (1) the rate constant k_1 (in pure chlorobenzene) was found equal to $0.28 \cdot 10^{-5} \text{ sec}^{-1}$. The constant k_2 of the bimolecular reaction was determined from the inclination of the line (Fig 1) to equal $1.65 \cdot 10^{-6} \text{ mol}^{-1} \cdot \text{sec}^{-1}$. The authors show the agreement of the effective constant $k_{\text{eff}} = k_1 + k_2 [\text{RH}]$ found in reference 2 with these values. The dependence of the reaction constant k_2 on the type of solvent was further studied in solutions of iso-decane, ethyl benzene and methyl oleate in chlorobenzene. The experimental results are likewise graphically

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The Mechanism of Chain Branching in the Reaction
of the Oxidation of n-Decane

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represented in figure 1. The values for k_2 show that the reaction rate increases in the same sense as the oxidizability of the hydrocarbon; that is, it increases with the decreasing stability of the C-H bond of the hydrocarbon. The authors mention a paper by N. N. Semenov (Ref 4). There are 1 figure and 6 references, 4 of which are Soviet. ✓

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

SUBMITTED: January 3, 1960

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81728

S/020/60/133/01/40/070

B004/B007

5.3200

AUTHORS: Blyumberg, E. A., Zaikov, G. Ye., Mayzus, Z. K., Emanuel', N. M., Corresponding Member of the AS USSR

TITLE: The Differences in the Oxidation Mechanism of Ethyl Alcohol in the Liquid and in the Gaseous Phase

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 133, No. 1, pp. 144 - 147

TEXT: In the preceding papers (Refs. 1, 2) some of the authors found that the oxidation of n-butane in the liquid state is more advantageous than in the gaseous state. In the liquid state, the reaction develops at lower temperature and at a high rate, it is more selective and such products of an intensive oxidation as are characteristic of the reaction in the gaseous phase lack nearly entirely. N. N. Semenov (Ref. 3) explained this difference by a change in the ratio of two competitive reactions:
 $RO_2 \longrightarrow R'O + R''OH$ (1) and $RO_2 + RH \longrightarrow RO_2H + R'$ (2). Low pressure and high temperature are intended to promote the course of reaction (1), high pressure and low temperature are expected to promote that of reaction (2). ✓

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The Differences in the Oxidation Mechanism of Ethyl Alcohol in the Liquid and in the Gaseous Phase S/020/60/133/01/40/070
B004/B007

For the purpose of checking this assumption, the authors investigated the oxidation of ethanol in the liquid phase (200°C, 50 atm) and in the same autoclave also the oxidation in the gaseous phase at reduced pressure (20 atm). The results of both reactions are compared in Fig. 1. The following characteristic features for these two reactions were observed.

1) Liquid phase: No induction period, high acetic acid- and ethyl acetate yield, low yield of CO, small quantities of acetic aldehyde, which appears only as an intermediate product. 2) Gaseous phase: Long induction period (10 h), slow course of reaction, little acetic acid and ethyl acetate, much CO, and acetic aldehyde as the main product. Formic acid and peroxide in both cases form in only small quantities, because they are not stable under the experimental conditions selected. The authors discuss these results on the basis of reaction equations. As the concentration of alcohol under the experimental conditions in transition from the liquid to the gaseous phase is reduced only to 1/5, this alone cannot be the cause of such a difference in the course of the reaction. By calculating the ratio k_2/k_1 of the rate constants of the reactions (1) and (2), they find that k_2/k_1 , in transition from the liquid to the gaseous phase, does not

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The Differences in the Oxidation Mechanism of
Ethyl Alcohol in the Liquid and in the Gaseous
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B004/B007

change by the five-fold but a thousand-fold. The main factor of the difference in the course of the reaction is therefore not the greater density of the liquid phase, but a specific behavior of the liquid phase, which may be caused either by intermolecular hydrogen bonds or by the reaction of ions lacking in the gaseous phase. There are 1 figure and 4 Soviet references.

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

SUBMITTED: March 29, 1960

Card 3/3

MAYZUS, Z.K.; EMANUEL', N.M.

Initiating action of nitrosyl chloride in the oxidation of propane. Dokl.AN SSSR 133 no.3:627-629 J1 '60.

(MIRA 13:7)

1. Institut khimicheskoy fiziki Akademii nauk SSSR. 2. Chlen-korrespondent AN SSSR (for Emanuel').
(Nitrosyl chloride) (Propane)

S/020/60/135/002/024/036
B004/B056

AUTHORS: Gagarina, A. B., ~~Mayzus, Z. K.~~, and Emanuel', N. M.,
Corresponding Member of the AS USSR

TITLE: Critical Phenomena in the Action of Inhibitors Upon
Degenerately Branched Chain Reactions

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 2,
pp. 354-356

TEXT: The authors studied the influence of various parameters of a reaction upon its course. For degenerately branched chain reactions in the gaseous phase, N. N. Semenov (Ref. 1) derived the critical conditions under which inflammation of the gases occurs. A study of the oxidation of n-decane in the presence of copper stearate (Ref. 6) showed that critical phenomena may occur also in the liquid phase. It was the purpose of the present work to prove the existence of critical concentrations of inhibitors in the oxidation of hydrocarbons, and to measure these concentrations. The authors investigated the oxidation of n-decane at a

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Critical Phenomena in the Action of
Inhibitors Upon Degenerately Branched Chain
Reactions

S/020/60/135/002/024,036
B004/B056

constant concentration of the inhibitor α -naphthol. The inhibitor was added two hours after the oxidation had begun, when the concentration of the hydroperoxides had attained 0.17 mole%. The concentration of α -naphthol was checked with a spectrophotometer. From Fig. 1 it may be seen that at α -naphthol concentrations between $8.2 \cdot 10^{-7}$ and $3.3 \cdot 10^{-7}$ mole/l, the oxidation of n-decane is nearly entirely inhibited. If the α -naphthol content drops from $3.3 \cdot 10^{-7}$ to $3.1 \cdot 10^{-7}$, an autocatalytic oxidation occurs such as occurs even if there is no inhibitor. There are 1 figure and 8 references: 5 Soviet, 1 US, and 2 British. ✓

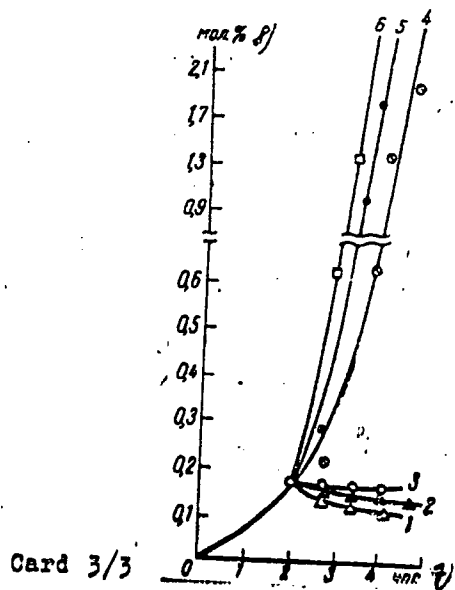
ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics of the Academy of Sciences USSR)

SUBMITTED: July 22, 1960

Card 2/3

Critical Phenomena in the Action of
Inhibitors Upon Degenerately Branched Chain
Reactions

S/020/60/135/002/024/036
B004/B056



Legend to Fig. 1: The kinetic curve of
the accumulation of hydroperoxides in
the oxidation of n-decane at 130°C and
various concentrations of α -naphthol
expressed in mole/l

- 1: $8.2 \cdot 10^{-7}$, 2: $4.4 \cdot 10^{-7}$, 3: $3.3 \cdot 10^{-7}$,
- 4: $2.9 \cdot 10^{-7}$, 5: $3.1 \cdot 10^{-7}$, 6: $1.0 \cdot 10^{-7}$;
- 7) hours, 8) mole%.

S/195/61/002/004/006
E111/E585

AUTHORS: Mazus, Z. N., Skibida, I. P. and Immet', A. N.

TITLE: Peculiarities of the kinetics of the oxidation of n-decane in open systems

ORIGINAL: kinetika i kataliz, v.2, no.4, 1961, 533-546

TEXT: The authors point out that most published information on chemical kinetics relates to closed systems, i.e. those without mass exchange with the surroundings. They have previously reported, together with Ye. I. Denisov (Ref.7: Dokl. AN SSSR, 128, 753, 1959), on autocatalytic reaction in an open system. For the present work they selected the oxidation of n-decane, which is interesting as a complicated reaction giving a comparatively large number of intermediate products. The oxidation was carried out at 140°C in the apparatus shown in Fig.1 (1 - syringe for adding reactants, 2 - tube to maintain a constant level for the reacting mixture, 3 - stopcock for sampling). The decane was poured into the vessel and oxidized in a closed system to a certain degree; thereafter n-decane was added at a constant rate, the volume of liquid in the vessel being kept constant by continuous removal through tube 4. card 1/64

peculiarities of the kinetics ...

2/195/83/001/01/2/000000
011/4537

(Fig. 1) The rate of decane addition v was taken as the ratio of the volume of liquid added per hour to that of the liquid in the vessel. This was varied from 0.0625 to 1.75 hour⁻¹. Samples taken periodically, were analyzed for hydrocarbons, alcohols, ketones, and acids. For a given temperature and addition rate, there can be only one stationary state. Fig. 1 shows concentration curves for alcohols (α), ketones (β) and acids (γ), respectively, as functions of time for various values of v . The numbers on the curves correspond to the various values of v : 1 - $v = 0.0625$, 2 - $v = 0.125$, 3 - $v = 0.1875$, 4 - $v = 0.25$, 5 - $v = 0.3125$, 6 - $v = 0.375$, 7 - $v = 0.4375$, 8 - $v = 0.5$, 9 - $v = 0.5625$, 10 - $v = 0.625$, 11 - $v = 0.6875$, 12 - $v = 0.75$. The author notes the mathematical relations between these curves and the concentration of acids, ketones, and alcohols, and hyperbolic functions of v (curves 1 and 2, respectively, for "low" and "high" values of v). From their own experiments, the author concludes that these effects can be explained by the



Peculiarities of the kinetics ...

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E111/E585

respectively, their stationary concentration by \bar{x} and \bar{y} and their initial concentrations by x_0 and y_0 , the authors show that a "false start" effect can occur at values of

$$v < \frac{k_1 \Delta x_0}{\Delta y_0} - k_2$$

with $\Delta x_0 > 0$ and $\Delta y_0 > 0$ or $\Delta x_0 < 0$ and $\Delta y_0 < 0$.

Here $\Delta x_0 = x_0 - \bar{x}$ and $\Delta y_0 = y_0 - \bar{y}$. "Overshoot" can occur at all the values of v if $\Delta x_0 > 0, \Delta y_0 < 0$ or $\Delta x_0 < 0$ and $\Delta y_0 > 0$.

The sign of the differential $(d\Delta y/dt)_{t=t_0}$ is determined only by

the sign of Δx_0 . Fig.6 shows the rules of accumulation of hydroperoxides and acids (curves 1, 2, respectively, left-hand ordinate) and of ketones and acids (curves 3, 4, respectively, right-hand ordinate) as functions of v (hours⁻¹). These curves show that by changing v the relative yields of the components can be changed. In general the maximum rate of accumulation of component c in

$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$ occurs at greater values of v than if the

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Peculiarities of the kinetics ...

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E111/E585

last stage were absent. Furthermore, except when $k_3 \gg k_2$, the maximum rate of accumulation of each successive product is attained at values of v less than that corresponding to the maximum rate of accumulation of the preceding product. The conclusion can be drawn that acids are not formed in n-decane oxidation from ketones and alcohols. In an open system the alcohols, ketones and acids are formed directly from hydroperoxides, but for a closed system L. S. Vartanyan, together with the present authors Z. K. Mayzus and N. M. Emanuel, have shown (Ref.8: Zh.fiz.khimii, 30, 862, 1956) that the acids are formed from hydroperoxides via an intermediate stage of ketone formation. There are 6 figures and 11 references. 9 Soviet-bloc and 2 non-Soviet-bloc. The English-language references read as follows: Ref.4: K. G. Denbigh, M. Hicks, F. M. Page, Trans. Faraday Soc., 44, 479, 1948; Ref.10: L. J. Durham, H. S. Mooser, J. Amer. Chem. Soc., 80, 327, 1958.

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

SUBMITTED - February 7, 1961

Card 4/64

S/020/61/140/001/010/024
B127/B101

AUTHORS: Gagarina, A. B., Mayzus, Z. K., and Emanuel', N. M. ,
Corresponding Member AS USSR

TITLE: Critical phenomena in hydrocarbon oxidation in the presence
of inhibitors in open systems

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 1, 1961, 153 - 156

TEXT: The authors referred to N. N. Semenov (O nekotorykh problemakh khimicheskoy kinetiki i reaktsionnoy sposobnosti - Some problems of chemical kinetics and reactivity, Izd. AN SSSR, 1958, p. 632) who showed that a critical concentration of inhibitors affects the oxidation process considerably. At a concentration lower than the critical one, the process is selfaccelerated, while at a higher concentration it becomes steady. The mathematical analysis was carried out by V. M. Andreyev. In this paper, the authors published the experimental studies. Their method is described in Ref. 5: Ye. T. Denisov, Z. K. Mayzus, I. P. Skibida, N. M. Emanuel', DAN, 128, 755 (1959). The oxidation was conducted by bubbling oxygen at 135°C through a mixture of n-decane with an inhibitor (α -naphthol). The process was checked by iodometric titration of the
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S/020/61/140/001/019/024
B127/B101

Critical phenomena in...

peroxides obtained. When the inhibitor concentration changes from $9 \cdot 10^{-9}$ to $9.05 \cdot 10^{-9}$ mole/ml, the steady hydroperoxide concentration drops sharply, practically to zero. The authors show that the critical inhibitor concentration depends on the peroxide concentration. The following

reactions constitute the total oxidation: $RH + O_2 \xrightarrow{\omega_0} R^{\cdot}$, chain formation.

Chain lengthening: $R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot}$ and $RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot}$. Cleavage:

$ROOH \xrightarrow{k_3} RO^{\cdot} + OH^{\cdot}$. Chain rupture: $RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_4}$ and $RO_2^{\cdot} + InH \xrightarrow{k_i} ROOH + In^{\cdot}$

(In = inhibitor). According to V. M. Andreyev who obtained

$$[InH]_{kp} = 2 \sqrt{\frac{2u_2 k_3 \omega_0}{k_i v (k_2 + v)} + \frac{2u_2 k_3}{k_i (k_2 + v)} + \frac{\omega_0}{v}} \quad (A)$$

for the critical inhibitor concentration and

$$\frac{k_i}{k_3} = \frac{2[RH] k_2}{k_2 + v} \frac{1}{(\sqrt{[InH]_{kp}} - \sqrt{\omega_0/v})^2} \quad (B)$$

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Critical phenomena in...

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($k_p = cr$) for the ratio. The authors determined the ratio k_1/k_2 for α -naphthol as an inhibitor, using the experimentally determined constant: $[InH]_{cr} = 9 \cdot 10^{-9}$ mole/ml, and the following constants: $v = 0.5 \text{ hr}^{-1}$, $[RH] = 5.2 \cdot 10^{-3}$ mole/ml, $\omega_0 = 1.8 \cdot 10^{-9}$ mole/ml. It was found that $k_1/k_2 = 1.33 \cdot 10^5$. The activation energy of the reaction of RO_2^{\cdot} with n-decane equals 15.1 kcal/mole, and that of the reaction of RO_2^{\cdot} with α -naphthol equals 5.4 kcal/mole. v is determined by W/V . W is the volume of the substance entering the reaction vessel per unit time, and V is the volume of the reaction mixture. There are 3 figures and 7 Soviet references. ✓

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

SUBMITTED: May 20, 1961

Card 3/3

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S/020/61/140/002/019/023
B130/B110

AUTHORS: Zaikov, G. I., Mayzus, Z. K., and Emanuel, N. M., Corresponding Member AS USSR

TITLE: Mechanism of chain ramifications during oxidation of methyl ethyl ketone in liquid phase

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 2, 1961, 405-408

TEXT: The authors found that the degenerate chain ramification during oxidation of methyl ethyl ketone (I) in liquid phase proceeds through the decomposition into radicals of two intermediate compounds, keto hydroperoxide and diacetyl. (I) was oxidized with atmospheric oxygen in an autoclave at 50 atm and 100-145°C. The oxidation products (acetic acid, ethyl acetate, diacetyl, ethanol, peroxides, CO, and CO₂) were analyzed chemically or by paper chromatography. From the course of the kinetic curve for the (I) consumption (Fig. 1) it may be concluded that the oxidation is a reaction of the first order. In fact, a complicated process takes place, which is suggested by the chain reaction and the anomalously low factor before the exponential function in the equation for the constant

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Mechanism of chain ramifications ...

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B130/B110

of the reaction rate, $k = 5.2 \cdot 10 \exp(11,200/RT) \text{ sec}^{-1}$. The chain character of the process was proven by addition of α -naphthol (II) as inhibitor. In the presence of (II), a noticeable induction period occurs, the duration of which rises with increasing inhibitor concentration. The rate of formation of chains during oxidation of (I) was determined from the kinetics of inhibitor consumption: $\omega_0 = 1.5 \cdot 10^{-6} \text{ mole/liter} \cdot \text{sec}$ at 145°C. During the process, the rate of initiation rises as compared with ω_0 due to the formation of degenerate ramifications. The rate of initiation during the reaction was determined by measuring the consumption of inhibitor (II) freshly supplied at different time intervals. Fig. 3 shows that the oxidation of (I) proceeds like a chain reaction. The rate of initiation, however, rises to double its value only. For the rate ω of oxidation of (I), it is written down: $\omega = (k_2/\sqrt{k_5})[RCOR_1]\omega_i^{1/2}$. An increase of the reaction rate ω to double its value changes the initiation rate $\omega_i^{1/2}$ by the 1.3-fold only, which leads to a linear dependence of the reaction rate on the concentration of (I), i.e., to a reaction of the first order. The rate of chain ramification during oxidation of (I) rises in proportion with the accumulating amount of keto hydroperoxide only at the

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B130/B110

Mechanism of chain ramifications ...

beginning of the reaction. Later on, a higher total rate of formation of radicals is observed than corresponds to the decomposition of keto hydroperoxide into free radicals. This shows that, besides keto hydroperoxide, other intermediates participate in the chain ramification during oxidation of (I). The assumption of a cooperation of diacetyl (formed in this reaction and readily decomposable into two radicals) was confirmed by an increasing rate of chain ramification on addition of diacetyl. The dependence of the ramification rate on the total concentration of keto hydroperoxide and diacetyl is calculated:

$$\omega_1 = k_1 [D]_1 + k_2 [P]_1 = k_1 \left\{ [D]_1 + \frac{k_2}{k_1} [P]_1 \right\} \quad (1).$$

Here, ω_1 is the rate of initiation at a certain instant of the reaction; $[D]$ and $[P]$ are the concentrations of diacetyl and keto hydroperoxide. On admixture of an additional amount of diacetyl, Eq. (1) obtains the form:

$$\omega_2 = k_1 [D]_2 + k_2 [P]_1 = k_1 \left\{ [D]_2 + \frac{k_2}{k_1} [P]_1 \right\} \quad (2).$$

From (1) and (2), we obtain:

$$\omega_1/\omega_2 = \left\{ [D]_1 + \frac{k_2}{k_1} [P]_1 \right\} / \left\{ [D]_2 + \frac{k_2}{k_1} [P]_1 \right\} \cdot k_2/k_1, \text{ can easily be}$$

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calculated since the other data are experimentally determined. The authors found for k_1 at 145°C : $1.0 \cdot 10^{-5} \text{ sec}^{-1}$, for k_2 : $1.4 \cdot 10^{-4} \text{ sec}^{-1}$. X

There are 4 figures and 14 references: 11 Soviet and 3 non-Soviet. The three references to English-language publications read as follows: W. D. Emmons, G. B. Lucas, J. Am. Chem. Soc., 77, 2287 (1955); J. S. F. Pode, W. A. Waters, J. Chem. Soc., 1956, 717; W. A. Waters, J. Chem. Soc., 1946, 1151.

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

SUBMITTED: May 20, 1961

Fig. 1. Kinetic curves for the consumption of methyl ethyl ketone and the accumulation of reaction products at $T = 145^\circ\text{C}$, pressure = 50 atm, and air velocity = 20 liters/hr. (1) Consumption of methyl ethyl ketone, (1') semi-logarithmic anamorphosis of curve 1, (2) accumulation of acetic acid, (3) CO_2 , (4) CO , (5) ethyl acetate, (6) diacetyl, (7) keto hydroperoxide (right-hand scale), (8) ethanol (right-hand scale).

Legend: (a) hr, (b) mole%.

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S/062/62/000/007/002/013
B117/B180

AUTHORS: Zaikov, G. Ye., and Mayzus, Z. K.

TITLE: Reasons for the different mechanism of oxidation of organic substances in gas or liquid phases

PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk, no. 7, 1962, 1175 - 1184

TEXT: Methods described in previous papers (E. A. Blyumberg, G. Ye. Zaikov, and N. M. Emanuel', Dokl. AN SSSR: 139, 99 (1961); Neftekhimiya 1, 235 (1961); E. A. Blyumberg, G. Ye. Zaikov, Z. K. Mayzus, and N. M. Emanuel', Dokl. AN SSSR 133, 144 (1960); Kinetika i kataliz 1, 510 (1960); G. Ye. Zaikov and Z. K. Mayzus, Kinetika i kataliz (1962); E. A. Blyumberg, Z. K. Mayzus, and N. M. Emanuel', sb. "Okisleniye uglevodorodov z zhidkoy faze" ("Oxidation of hydrocarbons in the liquid phase"), Izd. AN SSSR, M., 1959, p. 125; G. Ye. Zaikov, Zh. analit. khimii 15, 104 (1960); 15, 639 (1960); 17, 117 (1962)) were used to study the oxidation of ethyl alcohol and methyl-ethyl ketone with different amounts of benzene. Experiments with ethyl alcohol: 200°C, 50 atm., alcohol : benzene ratio

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S/062/62/000/007/002/013
B117/B180

Reasons for the different mechanism...

= 8 : 1, 2 : 1, 1 : 1, 1 : 2, and 1 : 3. Experiments with methyl-ethyl ketone: 145°C, 50 atm., ketone : benzene ratio = 1 : 1, 1 : 2, 1 : 3. In both cases, an increase in benzene, which reduces the dielectric constant of the medium, was found to alter the composition of reaction products. With ethyl alcohol, the amount of products obtained from the bimolecular reaction of peroxide radicals was 20% at 1 : 3, and 80% in pure alcohol. With methyl-ethyl ketone, (1 : 3) the reaction products had the same composition as with oxidation in the gas phase. Differences in the oxidation mechanisms of polar organic compounds in gas and liquid phases are due to the rate of the reaction between the peroxide radical and the oxidizing substance (bimolecular reaction), the dielectric constant of the medium, and the formation of intermolecular hydrogen bonds. The bimolecular reaction between RO_2^{\cdot} and the test material, is between two dipoles and slows down as polarity decreases. Good agreement between experimental and calculated dipole moments confirms the structure assumed for the activated complexes in the case of methyl-ethyl ketone, but not for ethyl alcohol. This shows that the reaction rate of RO_2^{\cdot} and ethyl alcohol is not only dependent on the polarity of the medium but also on

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S/062/62/000/007/002/013
B117/B180

Reasons for the different mechanism...

the formation of intermolecular hydrogen bonds. It is not the individual molecules (RH and RO_2^{\cdot}) which react, but aggregates consisting of five or more particles linked by hydrogen bonds. There are 5 figures and 3 tables.

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

SUBMITTED: January 30, 1962

Card 3/3

S/195/62/003/006/002/011
E075/E436

AUTHORS: Zaykov, G.Ye., Mayzus, Z.K.

TITLE: Oxidation of methylethylketone in the liquid and gaseous phases

PERIODICAL: Kinetika i kataliz, v.3, no.6, 1962, 846-854

TEXT: A comparative study of the mechanism of oxidation of methylethylketone in the liquid and gaseous states was undertaken to elucidate the effect of polarity and the absence of hydrogen bonding in the oxidized molecules. The liquid phase oxidation was studied for the first time. Both the liquid and gaseous oxidation were carried out at 145°C and 50 atm. The liquid oxidation was a complex chain reaction imitating a first order reaction. Individual stages of the reactions were studied by adding α -naphthol at various times during the reaction, this stopped the chain reactions and permitted to characterize the non-chain reactions. Diacetyl, ketohydroperoxide and ethylacetate (intermediate oxidation products) undergo non-chain decomposition, the hydroperoxide in this case decomposing much more rapidly than hydrocarbon hydroperoxides. Diacetyl decomposes
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Oxidation of methylethylketone ...

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E075/E436

at a higher rate than that calculated from the consumption of α -naphthol which indicates that the branching reaction is not the only decomposition process. Ethylacetate is decomposed by water forming during the oxidation, acetic acid thus produced being a part of the total acid formed. The remainder of the acid is formed from the decomposition of diacetyl. Acetic acid is also formed from ketohydroperoxide via diacetyl. In the gaseous phase oxidation there is formation of formaldehyde, acetaldehyde, acetone, formic acid, methyl acetate, methyl alcohol and CO, which are not produced in the liquid phase oxidation. Conversely, the formation of ethylacetate and diacetyl decreases during the gaseous oxidation. There is little difference however in the formation of acetic acid. Comparing the rates of formation of the oxidation products during the two types of oxidation, the authors conclude that the specificity of the liquid phase oxidation is due to the polarity of the oxidized substance. Comparison with the oxidation of ethyl alcohol indicates that hydrogen bonds also affect the mechanism of oxidation. The mechanism of chain branching is the same for the liquid and gaseous oxidations which
Card 2/3

Oxidation of methylethylketone ...

S/195/62/003/006/002/011
E075/E436

indicates that the polarity of the oxidized substance affects all the stages of the oxidation process. There are 6 figures and 2 tables.

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

SUBMITTED: October 7, 1961

Card 3/3

S/020/62/143/002/016/022
B145/B138

AUTHORS: Mayzus, Z. K., Emanuel', N. M., Corresponding Member AS USSR,
and Yakovleva, V. N.

TITLE: Mechanism of chain formation in n-decane oxidation

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 143, no. 2, 1962, 366 - 369

TEXT: The mechanism was experimentally investigated for liquid-phase n-decane to find out whether the reaction concerned is trimolecular ($2 \text{RH} + \text{O}_2 \rightarrow \text{R}^\bullet + \text{H}_2\text{O}_2 + \text{R}^\bullet - q_2$) or bimolecular ($\text{RH} + \text{O}_2 \rightarrow \text{R}^\bullet + \text{HO}_2^\bullet - q_1$). The chain formation rate W_0 was measured with α -naphthene as inhibitor, whose concentration was measured by spectrophotometry after reaction with p-nitrobenzodiazonium chloride to form an azo dye at 150°C. The inhibitor consumption is linearly time-dependent up to a 30 - 40% conversion. The rate of inhibitor consumption, W_{InH} , determined from the foregoing, grows with the inhibitor concentration, i. e., the radical formation rate is so low at the beginning of oxidation as to become

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Mechanism of chain ...

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comparable to the rate of inhibitor oxidation by O_2 . The resulting equation reads: $-d[InH]/dt = W_0 + k_i [InH]^n [O_2]$. W_{InH} is linearly dependent on $[InH]^2$ ($n=1.95$ was found from the straight line in the coordinates $d[InH]/dt, \log [InH]$). $W_0 = 2.6 \cdot 10^{-9}$ mole/liter·sec was determined from section cut off by the straight-line on the ordinate of the $W_{InH} - [InH]^2$ diagram, and $k_i = 1.2 \cdot 10^{-1}$ liter²/mole²·sec from the slope. The same value for k_i was also found when oxidizing with a 53% O_2 + 47% N_2 mixture. Measurements at different partial pressures of O_2 and of n-decane - p-dichloro benzene mixtures of various compositions showed the chain formation reaction to be of first order with respect to the O_2 concentration, and of second order with respect to the decane concentration.

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B145/B138

Mechanism of chain ...

$k_i = 5.2 \cdot 10^{-1}$ liter²/mole²·sec, i. e. a higher value, was established in the reaction in n-decane - p-dichloro benzene mixtures, evidently due to the polarity of the solvent. There are 3 figures and 7 references: 6 Soviet and 1 non-Soviet. The reference to the English-language publication reads as follows: C. A. Mc Dowell, J. H. Thomas, J. Chem. Phys., 17, 558 (1949).

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

SUBMITTED: December 11, 1961

Card 3/3

SKIBIDA, I.P.; MAYZUS, Z.K.; EMANUEL', N.M.

Study of kinetic regularities of complex chain processes as a method for determining the rates of formation and consumption of intermediate products. Dokl. AN SSSR 144 no.1:170-172 My '62. (MIRA 15:5)

1. Institut khimicheskoy fiziki AN SSSR. 2. Chlen-korrespondent AN SSSR (for Emanuel').
(Hydrocarbons) (Chemical reaction, Rate of) (Oxidation)

KA.PUKHINA, G.V.; MAIZUS, Z.A.

Studying the liquid-phase oxidation of n-levone using gas-liquid chromatography. *Khimiya i biokhimiya* 2 no. 1901-1905 1962. (1962) 1-1

1. Institut Khimicheskoy Fiziki AN SSSR.

L 17061-63 EPR/EPF(c)/EWP(q)/EWT(m)/BDS S/062/63/000/004/005/022
AFFTC Ps-4/Pr-4 RM/WW/JD 68
AUTHOR: Mayzus, Z. K. and Privalova, L. G. 66
TITLE: Importance of reaction products in the mechanism of n-decane 7
 oxidation 7
PERIODICAL: Akademiya nauk SSSR. Izvestiya. Otdeleniye khimicheskikh nauk,
 no. 4, 1963, 628-633

TEXT: In a continuation of work in the field, the effect of alcohol additives on the formation rate and consumption of hydrogen peroxides was studied and measurements were made of these rates for deeper oxidation of n-decane. By means of the kinetic isotope method it was found that in the liquid phase oxidation of n-decane there initially occurs an increase of the rates of formation and consumption of hydrogen peroxides, later a decrease of these rates, again changing their growth. The observable changes in the process mechanism are explained by the effect of the reaction products on the elementary stages of the extension and branching of the chains. The decrease in the rates of formation and consumption of hydrogen peroxides is associated with the

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L 17061-63

S/062/63/000/004/005/022

Importance of reaction products in the.....

2

decrease in activity of the radicals leading the chain process as a result of the interaction of the peroxide radical with alcohol. Increase of these rates after a minimum is explained by an acceleration of decomposition of hydrogen peroxides into radicals under the action of the acid formed in the reaction. There are 7 figures.

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

SUBMITTED: June 15, 1962

Card 2/2

8/020/63/148/006/021/023
B190/B102

AUTHORS: Skibida, I. P., Kulitskiy, Z. I., Mayzus, Z. K.

TITLE: Reactivity of isomeric decanols, the intermediates of n-decane oxidation

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 148, no. 6, 1963, 1358-1360

TEXT: The reactivity of decanols with hydroperoxides was determined from their consumption when added to the reaction mixture. The pure initial product n-decane was added to the reaction mixture at a certain rate until a stationary concentration C_1 of the intermediate (alcohol) set in.

A mixture of decane and 0.205 mole/l of decanol-2 was added at the same rate, whereupon a higher stationary concentration C_2 of the intermediate became established. If, instead of this mixture, mixtures of decanol-4 and subsequently of decanol-5 having the same concentration were added, then the stationary concentration C_2 remained constant. The hydroperoxide concentration also remained constant during the experiments. Hence it

Card 1/2

Reactivity of isomeric decanols, ...

S/020/63/148/006/021/023
B190/B102

follows that the decanols used exert no effect on the radial concentration in the system and have the same reactivity. The gross velocity of the formation of the alcohols in n-decane oxidation was found to be

$$v_{gr} = 7.4 \cdot 10^{-4} \text{ mole/l min.}$$

There is 1 figure.

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

PRESENTED: July 28, 1962, by V. N. Kondratyev, Academician

SUBMITTED: July 23, 1962

Card 2/2

SKIBIDA, I.P.; MAYZUS, Z.K.; EMANUEL¹, N.M.

Activation energy of the chain reactions by which alcohols are formed and consumed in the oxidation of n-decane. Dokl. AN SSSR 149 no.5:1111-1114 Ap '63. (MIRA 16:5)

1. Institut khimicheskoy fiziki AN SSSR. 2. Chlen-korrespondent AN SSSR (for Emanuel¹).
(Decane) (Alcohols) (Chemical reaction, Rate of)

ZAIKOV, G.Ye.; MAYZUS, Z.K.

Polarity of the medium as effecting the activation energy of the chain continuation reaction in the oxidation of ethyl alcohol and methyl ethyl ketone. Dokl. AN SSSR 150 no.1:116-119 My '63.
(MIRA 16:6)

1. Institut khimicheskoy fiziki AN SSSR. Predstavleno akademikom N.N.Semenovym.

(Ethyl alcohol) (Butanone) (Oxidation) (Activation energy)

L 19014-63

EPF(c)/EWP(j)/EWT(m)/BDS Pr-4/Pc-4 RM/WW/JW/MAY

ACCESSION NR: AP3007235

S/0020/63/152/001/0110/0113

AUTHOR: Karpukhina, G. V.; Mayzus, Z. K.; Emanuel', N. M.
(Corresponding member, AN SSSR)

72
68

TITLE: Interaction of two inhibitors in hydrocarbon oxidation

SOURCE: AN SSSR. Doklady*, v. 152, no. 1, 1963, 110-113

TOPIC TAGS: antioxidant, oxidation inhibitor, inhibitor, oxidation, hydrocarbon oxidation, hydrocarbon, synergism, synergistic effect, synergistic inhibitor, Neozone D, 2-naphthylamine, N-phenyl-, phenol, 2,6-di-tert-butyl-, benzene, ethyl-, isobutyronitrile, azodi-, Ionol, p-cresol, 2,6-di-tert-butyl-, phenolphthalein, tetraisopropyl-, diphenylamine, inhibitor consumption, consumption rate, free radical, hydrazine, tetraphenyl-

ABSTRACT: The consumption rate of two inhibitors (antioxidants) of the phenol and aromatic amine type in hydrocarbon oxidation has been studied to clarify the mechanism of the synergistic effect of two inhibitors used simultaneously. Neozone D (N-phenyl-2-naphthylamine) and 2,6-di-tert-butylphenol (I) were used both separately and simultaneously in ethylbenzene oxidation initiated with

Card 1/3

L 19014-63

ACCESSION NR: AP3007235

2

azobisisobutyronitrile¹ and conducted at 70C. This oxidation has the advantage of being an "unbranched" chain reaction. Changes in inhibitor concentration in the course of oxidation were determined spectrophotometrically by formation of an azo dye from the inhibitor and added diazotized p-nitroaniline. It was found that a single inhibitor is spent at a rate equal to one-half the initiation rate, indicating that one inhibitor molecule reacts with two RO_2 free radicals. When the two inhibitors are used together, consumption of Neozone D is slight until practically all of the phenol I is spent. Neozone D is subsequently consumed at a rate close to the half-rate. This amine-consumption inhibition is observed at various ratios and total contents of the two inhibitors. The same inhibition was observed with other pairs of phenols and amines; e.g., Neozone D with 2,6-di-tert-butyl-4-methylphenol (Ionol) or with tetraisopropylphenolphthalein. Replacement of Neozone D with another amine, diphenylamine, also resulted in considerable slowing of amine consumption in the presence of the phenol. In an attempt to explain this phenomenon, the rate constants of the reaction between inhibitor and RO_2 free radicals

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L 19014-63

ACCESSION NR: AP3007235

were determined by the chemiluminescence quenching method (O. N. Karpukhin, V. Ya. Shlyapintokh, N. V. Zolotova, Izv. AN SSSR, OKhN, 1963, No. 10). It was clearly indicated that inhibition of amine consumption in the presence of phenols is not caused by the difference in the values of the constants, i.e., in the effectiveness of the inhibitor. It is assumed that a free radical formed by the reaction of the amine with RO_2 radicals abstracts a hydrogen atom from the phenol, thus restoring the amine. Hence, amine concentration changes only slightly until all of the phenol is consumed. This assumption was confirmed experimentally by establishing that diphenylamine accumulates during ethylbenzene oxidation inhibited by Ionol and tetraphenylhydrazine. The latter is a source of $(C_6H_5)_2\dot{N}$ radicals which form diphenylamine on reacting with Ionol (by abstracting an H atom from this phenol). Oxidation of the $R_1R_2\dot{N}$ free radicals does not occur, since the reaction rate with Ionol is higher than the $R_1R_2\dot{N}$ oxidation rate. The results of the study may also contribute to an understanding of the synergistic effect of inhibitor pairs at higher temperatures. Orig. art. has: 4 figures and 1 table.

ASSN: Institute of Chemical Physics, Academy of
Sci. USSR

Card 3/103

EMANUEL', N.M.; DRONOVA, L.M.; KONOVALOVA, N.P.; MAYZUS, Z.K.;
SKIBIDA, I.P.

Antileukemic effect of 2,6-di-tert.-butyl-4-methylphenol
(ionol). Dokl. AN SSSR 152 no.2:481-484 S '63. (MIRA 16:11)

*

PRIVALOVA, L.G.; MAYZUS, Z.K.

Effect of organic acids on the mechanism of chain branching
during oxidation of decane. Iz. AN SSSR. Ser. khim. no. 2: 281-286
F '64.

(MIRA 17:3)

1. Institut khimicheskoy fiziki AN SSSR.

ACCESSION NR: AP4024407

S/0204/64/004/001/0082/0090

AUTHOR: Skibida, I. P.; Mayzus, Z. K.; Emanuel', N. M.

TITLE: Reactivity of intermediate materials in hydrocarbon oxidation reactions.

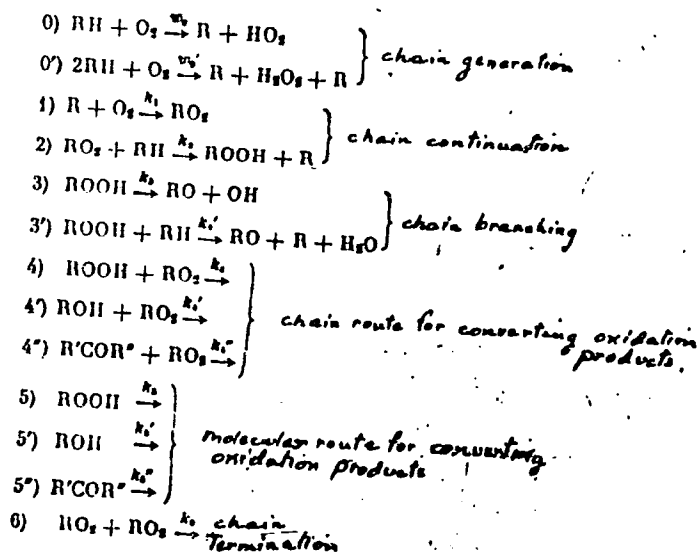
SOURCE: Neftekhimiya, v. 4, no. 1, 1964, 82-90

TOPIC TAGS: hydrocarbon oxidation, reaction rate, hydroperoxide, alcohol, ketone, RO sub 2 radical, ethylbenzene oxidation, decane oxidation, kinetics, acetophenone, methylphenylcarbinol, reactivity

ABSTRACT: The rates of reaction of hydroperoxides, alcohols and ketones with RO_2 radicals in the oxidation of ethylbenzene and n-decane were determined by a method developed by the authors (Uspekhi khimii 26, 416, 1957) wherein the rates of formation and consumption of reaction products in an open system may be determined. The various parallel and consecutive reactions by which the chain oxidation of hydrocarbons may proceed were investigated and the reaction rates determined;

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ACCESSION NR: AP4024407



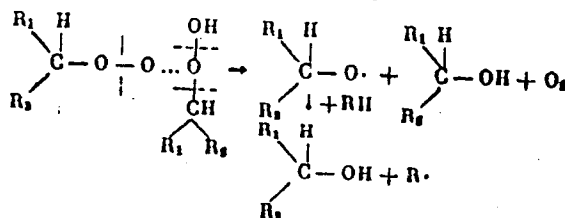
Card 2/8

ACCESSION NR: 4024407

The kinetic curves of ethylbenzene consumption and hydroperoxide accumulation (fig. 1) and alcohol (methylphenylcarbinol), hydroperoxide and ketone (acetophenone) accumulations (figs. 2 and 3) for reactions run at 118 C were drawn. Acetophenone is the end product of ethylbenzene oxidation; its rate of consumption $k_4''(\text{RO}_2) = 0$, $k_5 = 0$, and $k_3 = 0.82 \times 10^{-3}$ mol/l.hr. The reactivity of ethylbenzene and its oxidation products with RO_2 increases in the series ethylbenzene ($k_2 = 8.3 \times 10^{-3}$ hrs $^{-1}$), alpha-hydroperoxide ($k_4 = 7.8 \times 10^{-2}$ hrs $^{-1}$), and methylphenylcarbinol ($k_4' = 10.2 \times 10^{-2}$); the relative reactivities are 1:9.5:12. $k_6 = 7.8 \times 10^{10}$ l/mol.hr. The rate constants of the elementary reactions were determined: $k_2 = 1.3 \times 10^1$, $k_4 = 1.2 \times 10^2$ and $k_4' = 1.6 \times 10^2$ l/mol.sec. The reactivity of n-decane, its hydroperoxide and its isomeric alcohols formed by oxidation at 140 C was determined (fig. 4). The rate of reaction with RO_2 radicals for all the isomers is the same. $k_2(\text{RO}_2) = 3.8 \times 10^{-4}$ min $^{-1}$; $k_4'(\text{RO}_2) = 2.6 \times 10^{-3}$; $k_4(\text{RO}_2) = 0.51 \times 10^{-2}$; hence the rate of reaction of RO_2 increases in the order n-decene, alcohols, hydroperoxide in the ratio of 1:6.3:13. As with ethylbenzene, the reactivity of n-decane with the RO_2 radical is less than with their respective hydroperoxides or alcohols. Unlike ethylbenzene, the reactivity with the decyl alcohols is two times less than with the hydroperoxide, leading to the formation of different products, in this case alcohols;

Card 3/8

ACCESSION NR: AP4024407



Orig. art. has: 21 equations and 6 figures.

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

SUBMITTED: 26Jul63

DATE ACQ: 17Apr64

ENCL: 04

SUB CODE: GC

NO REF SOV: 007

OTHER: 001

Card 4/8

ACCESSION NR: AP4024407

ENCLOSURE: 01

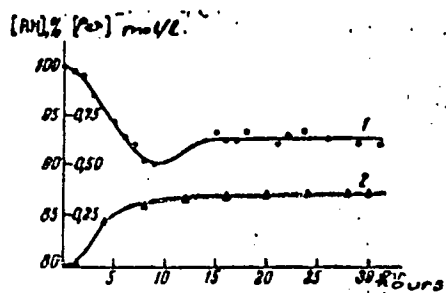


fig. 1

Kinetic curves of the consumption of hydrocarbon (curve 1, external scale) and accumulation of hydroperoxide (curve 2, internal scale). Ethylbenzene oxidized in open system $v/V = 0.102 \text{ hr}^{-1}$, 118° .

Card 5/8

ACCESSION NR: AP4024407

ENCLOSURE: 02.

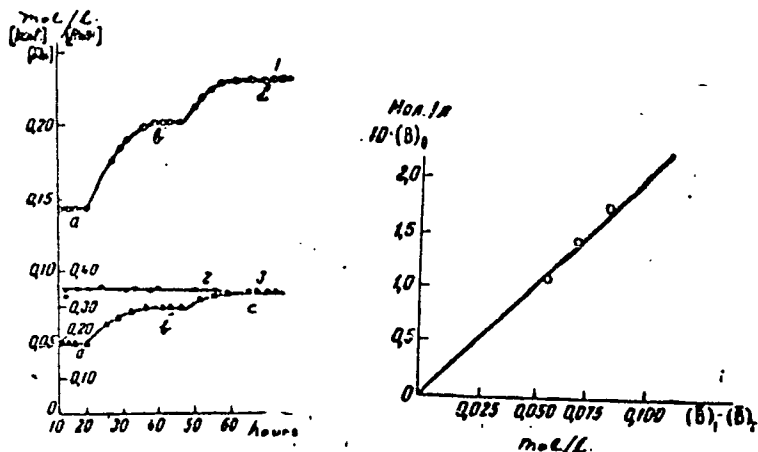


fig. 2

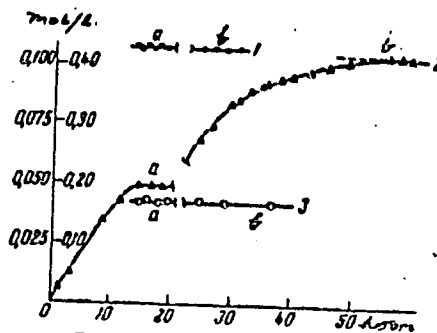
Kinetic curves for the accumulation of alcohol (1), hydroperoxide (2) and ketone (3). Ethylbenzene oxidation in open system with ethylbenzene feed (part a) and feed of methylphenylcarbinol solution in ethylbenzene, containing 0.106 mol/l alcohol (part b) and 0.17 mol./l. alcohol (part c). $v/V = 0.102 \text{ hr}^{-1}$, 118° .

Card 6/8

ACCESSION NR: AP4024407

ENCLOSURE: 03

Fig. 3. Kinetic curves for the accumulation of hydroperoxide, ketone and alcohol. Oxidation of ethylbenzene in open system with ethylbenzene feed (curves 1a, 2a, 3a) and feed of ethylbenzene containing 0.055 mol/l. acetophenone (curves 1b, 2b, 3b), 1--hydroperoxide (internal scale); 2--acetophenone; 3--methylphenylcarbinol. $v/V = 0.102 \text{ hr}^{-1}$.

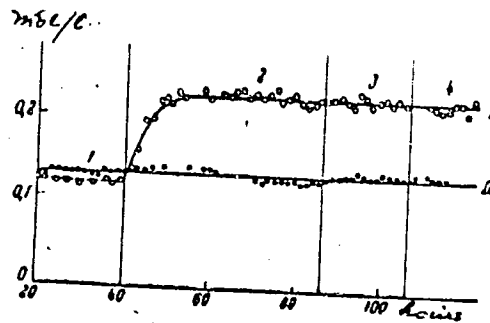


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ACCESSION NR: AP4024407

ENCLOSURE: 04

Fig. 4. Stationary concentration of alcohols (I) and hydroperoxide (II) in oxidizing n-decane in open system; $v/V = 2.7 \times 10^{-3} \text{ min}^{-1}$, 140° . Section 1--pure n-decane feed; 2--mixture of n-decane with decanol-2; in amount of 0.205 mol/l.; 3--mixture of n-decane with the same amount of decanol-4; 4--mixture of n-decane with decanol-5.



ard 8/8

ZAIKOV, G. Ye.; MAYZUS, Z.K.; EMANUEL', N.M.

Initiation of chains in the liquid-phase oxidation of methyl
ethyl ketone and ethyl alcohol. Neftekhimiya 4 no.1:91-95'64
(MIRA 17:6)

1. Institut khimicheskoy fiziki AN SSSR.

L 57867-65 EWI(m)/EPF(c)/ENP(j)/EWA(c) Pc-4/Pr-4 RPL JW/RM
ACCESSION NR: AP5016841 UR/0204/65/005/003/0394/0398
547.21:542.978

32
30
B

AUTHOR: Karpukhina, G. V.; Mayzus, Z. K.; Emanuel', N. M.

TITLE: Synergistic effect of inhibitors in hydrocarbon oxidation

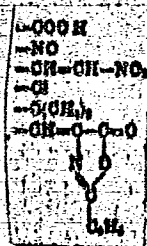
SOURCE: Neftekhimiya, v. 5, no. 3, 1965, 394-398

TOPIC TAGS: oxidation, inhibitor, synergism, amine, phenol ethylbenzene

ABSTRACT: The synergistic effect of an aromatic amine and 4-substituted 2,6-di-tert-butylphenol inhibitors in oxidation reactors has been studied. The inhibitor effectiveness of mixtures of N-phenyl-β-naphthylamine (Neozone D) and 2,6-di-tert-butyl-

phenols having the following 4-substituents

7

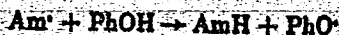


Card 1/3

L 57867-65

ACCESSION NR: AP5016841

or thiophenol in the reaction of azobisisobutyronitrile-initiated ethylbenzene oxidation at 60 and 70C was determined by chemical kinetics and luminescence methods. It was confirmed for all the above inhibitor pairs that synergism is exhibited which is due to the reaction of the amine free-radical formed with the phenol, regenerating the original amine:



All the phenols tested were inferior to Neozone D in inhibitor effectiveness. Therefore, the existence of such a synergistic effect makes it possible, when necessary, to substitute a poorer inhibitor for a more effective one without lowering the overall effectiveness below that of the better inhibitor. Orig. art. has: 5 figures, 1 table, and 2 formulas. [SM]

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

SUBMITTED: 27Jul64

ENCL: 00

SUB CODE: 00GC

NO REF SOV: 006

OTHER: 001

ATD PRESS: 4038

Card 2/2

ANDRONOV, L.M.; MAYZUS, Z.K.; EMANUEL', N.M.

Kinetics of oxidation of aqueous solutions of glyceraldehyde
by molecular oxygen. Izv. AN SSSR. Ser. khim. no.9:1519-
1523 '65. (MIRA 18:9)

1. Institut khimicheskoy fiziki AN SSSR.

L 35087-65 EWT(1)/EWT(m)/EPF(c)/EWP(j)/EWA(c) Pc-4/Pr-4 IJP(c)/RPL JW/EM

ACCESSION NR: AP5006703

S/0076/65/039/002/0498/0500

AUTHOR: Karpukhina, G. V.; Mayzus, Z. K.; Karpukhin, O. N.

TITLE: Chemiluminescence study of the interactions of two inhibitors during hydrocarbon oxidation

SOURCE: Zhurnal fizicheskoy khimii, v. 39, no. 2, 1965, 498-500

TOPIC TAGS: inhibitor interaction, chemiluminescence, oxidation inhibitor, phenol, naphthylamine, hydrocarbon oxidation, ethylbenzene

ABSTRACT: The simultaneous use of several inhibitors for the suppression of oxidation often appears to be significantly more effective than the separate use of any of the inhibitor components. The mechanism of the simultaneous action of two inhibitors is not yet fully clarified. In a recent paper (Dokl. AN SSSR, 152, 120, 1963), the authors studied the consumption kinetics of several pairs of inhibitors, one member of which belonged to the class of amines and the other to the phenols. It was found that the phenol inhibitor was consumed at the same rate as if it were alone, while the amine concentration remained unchanged as long as there was any phenol present. In the present paper, the authors show that the chemiluminescent method can be used for the study of the mechanism by which a mix-

Card 1/2

L 35087-65

ACCESSION NR: AP5006703

ture of inhibitors acts during the oxidation of hydrocarbons. Tests using this method confirmed the intensive interaction between N-phenyl- β -naphthylamine and 2,6-di-tertiary-butylphenol inhibitors during their simultaneous presence in the ethylbenzene oxidation reaction. Orig. art. has: 5 formulas and 2 figures.

ASSOCIATION: Institut khimicheskoy fiziki, Akademiya nauk SSSR (Physical chemistry institute, Academy of sciences, SSSR)

SUBMITTED: 02Apr64

ENCL: 00

SUB CODE: OC, CC

NO REF SOV: 003

OTHER: 000

Card 2/2

L 1654-66 EWT(m)/EPF(c)/EMP(j) RPL RM

ACCESSION NR: AP5021420

UR/0076/65/039/008/1965/1969
541.124/.128

AUTHOR: Privalova, L. G.; ⁴⁴⁵⁵Mayzus, Z. K.; ⁴⁴⁵⁵Denisov, Ye. T. ⁴⁴⁵⁵

42
39
B

TITLE: Effect of the oxidation products of n-decane on radical activity in the chain propagation reaction

SOURCE: Zhurnal fizicheskoy khimii, v. 39, no. 8, 1965, 1965-1969

TOPIC TAGS: decane oxidation, free radical, reaction rate, reaction kinetics, chain propagation

ABSTRACT: The purpose of the study was to determine the role of one of the intermediates (alcohol) in the chain propagation reaction involved in the oxidation of n-decane, its influence on the composition and activity of the radicals, and the contribution of the formation of the alcohol to the change in the overall oxidation rate of n-decane. To this end, the value of $w/\sqrt{w_i}$ [RH] (where w is the rate of the chain process of oxidation of the hydrocarbon and w_i the initiation rate of radicals) was measured in the course of oxidation of n-decane in experiments involving the addition of the alcohol (5-nonanol) and compared with the corresponding values

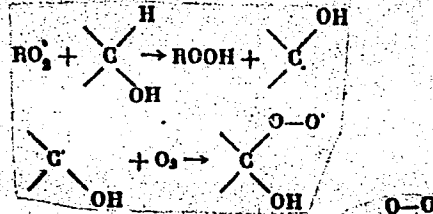
Card 1/3

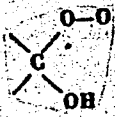
L 1654-66

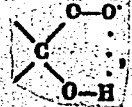
ACCESSION NR: AP5021420

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obtain during oxidation of n-decane without the addition of the products. Addition of the alcohol was found to decrease considerably the activity of the radicals propagating the oxidation chains. The radicals formed by the reaction of RO₂ with the alcohol are 5.2 times less active than the RO₂ radicals. The reaction of RO₂ with the alcohol may be represented as follows:



Thus, the RO₂ radical is substituted for the  radical. In the latter, an

intraradical hydrogen bond  may be formed which lowers the activity of this

Card 2/3

L 1654-66

ACCESSION NR: AP5021420

radical. Differences in the nature of the dependence of $\nu/\sqrt{w_1}[\text{RH}]$ on ROOH obtained from the experimental data and calculated by allowing for the effect of the alcohol indicate that the effect of the oxidation products of *n*-decane is not limited to the inhibiting influence of the alcohol, and that on the contrary, other products present in the reaction mixture have an accelerating effect on the oxidation process. The overall effect of all the oxidation products causes first an increase, then a decrease in the activity of the radicals. Orig. art. has: 3 figures and 9 formulas.

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

SUBMITTED: 29Jun64

4456
ENCL: 00

SUB CODE: GC

NO REF SOV: 012

OTHER: 000

Card 3/3 *PP*

L 40544-65 EWT(m)/EPF(c) Pr-4 RM
ACCESSION NR: AP5064204

3/0020/65/160/001/0158/0161

AUTHORS: Karpukhina, G. V.; Mayzus, Z. K.; Emanuel', N. M. (Corresponding member AN SSSR)

TITLE: On synergism mechanism with inhibitor mixtures in liquid phase oxidation reaction

SOURCE: AN SSSR. Doklady, v. 160, no. 1, 1965, 158-161

31
30
B

TOPIC TAGS: inhibitor, benzene, synergism, amine, reaction kinetics, chemiluminescence/ Neozone

ABSTRACT: To establish the connection between inhibitor interaction and synergism, the absorption kinetics of oxygen in ethyl-benzene/oxidation was studied in the presence of two inhibitors: Neozone-D-2,6-di-tertiary-butylphenol and Neozone-D-4-oxi-3,5-di-tertiary-butyl-n-nitrostyrene. Azoisobutyric acid was used as the initiator with rate (W_1) 2×10^{-7} mol/liter/second. The consumption progress of the inhibitor was also measured. It was shown that an interaction exists between the amine radical and the phenol, giving rise to amine regeneration. The amine is not consumed while the system still contains phenol. The ethyl-benzene oxidation

Card 1/3

L 40544-65

ACCESSION NO: AP5004204

retardation period T is shown graphically as a function of inhibitor concentration ratio. The results show that T , in the presence of the inhibitor mixture, departs from the law of addition in the direction of increased decelerating action of the inhibitor mixture. The mechanism of the inhibitor mixture action is discussed schematically under the condition that each one of the inhibitors reacts with two RO_2 radicals. From reaction concentration equations the expression

$$\frac{A-1}{2B^2} = \frac{k_5}{k_1 k_3 W_1} - A \frac{k_4}{k_2 k_3 W_1}$$

is obtained, where

$$A = \frac{d(\text{AmH})/dt}{d(\text{PhOH})/dt} \frac{k_2(\text{PhOH})}{k_1(\text{AmH})}; \quad B = k_1(\text{AmH}) + k_4(\text{PhOH})$$

The magnitudes of (AmH) and (PhOH) are determined experimentally. The above relationship is shown to be linear and provides means for determining the reaction constants $k_5/k_3 = 4 \times 10^{-4}$ and $k_6/k_1 = 9.5 \times 10^{-6}$. The experimental results also showed that $(RO_2) = 3.3 \times 10^{-9}$ mol/liter, and from chemiluminescence measurements it was found that $k_1 = 1.3 \times 10^5$ and $k_2 = 1.1 \times 10^5$. Thus, the hydrocarbon oxidation under the action of inhibitor mixtures is accompanied by amine reduction. Orig. art. has: 9 formulas and 3 figures.

Core 2/3 Submitted 28 Jul 64

L 53900-65 EWT(m)/EPF(c)/T/EWP(j) Pc-4/Pr-4 RPL RM

ACCESSION NR: AP5011540

26
28 UR/0020/65/151/005/1135/1137

AUTHORS: Privalova, L. G.; Mayzus, Z. K.; Emanuel', N. M. (Corresponding member AN SSSR)

TITLE: The mechanism of forming free radicals during decomposition of hydroperoxides by organic acids

SOURCE: AN SSSR. Doklady, v. 161, no. 5, 1965, 1135-1137

TOPIC TAGS: hydroperoxide, free radical, chain structure, oxidation

ABSTRACT: Investigation of chain splitting in the oxidation of n-decane has shown that at relatively slight conversion of the n-decane the formation of radicals proceeds by two parallel reactions: by monomolecular decomposition of hydroperoxide and by bimolecular reaction between hydroperoxide and the original hydrocarbon. As the depth of oxidation increases, the splitting mechanism becomes more complex. The accumulation of organic acids (among the reaction products) leads to a marked increase in rate of hydroperoxide decay to radicals. It has been proposed that the radicals form by decomposition of an intermediate complex between the hydroperoxide and the acid, forming by development of intermolecular hydrogen bonds. To test this, the authors investigated the dependence of decomposition rate on acid

Card 1/2

L 53900-65

ACCESSION NR: AP5011540

concentration. The tests were carried out in an oxidation chamber and were made at 100, 110, 120, 140, and 150C. Oxidized n-decane was placed in the chamber and brought to one of the desired temperatures. Alpha naphthol was then added in sufficient quantity to cause complete suppression of chain decomposition of the hydroperoxide. The dependence curve was found to level off, showing that the rate of decomposition reaches a point beyond which it no longer depends on acid concentration, and this means that the splitting takes place through intermediate formation of a complex that then breaks down to free radicals. The authors conclude that at deep stages of oxidation, when organic acids accumulate in considerable quantities in the reaction mixture, the reaction between hydroperoxide and acid, with the formation of free radicals, becomes the principal reaction in the splitting of chains. Orig. art. has: 5 figures, 1 table, and 6 formulas.

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

SUBMITTED: 23Dec64

ENCL: 00

SUB CODE: 00, 00

NO REF SOV: 008

OTHER: 002

Card 2/2

MAYZUS, Z.K.; SKIBIDA, I.P.; EMANUEL', N.M.

Mechanism of the catalytic decomposition of hydroperoxides
under the effect of copper stearate. Dokl. AN SSSR 164
no.2:374-377 S '65. (MIRA 18:9)

1. Chlen-korrespondent AN SSSR (for Emanuel').

L 112118-66 EMT(m)/TMP(1)/T IJP(c) MW/MW/INT/AM

ACC NR: AP6021960

SOURCE CODE: UR/0030/66/000/006/0076/0080

AUTHOR: Mayzus, Z. K. (Candidate of chemical sciences)

ORG: none

TITLE: Symposium on chain and free-radical reactions

SOURCE: AN SSSR. Vestnik, no. 6, 1966, 76-80

TOPIC TAGS: chemical conference, radical polymerization, oxidation kinetics, chemical personnel, free radical, chain reaction, chemical reaction, reaction mechanism, polymerization kinetics, chemical detection, chemical synthesis

ABSTRACT: A symposium on chain and free-radical reactions was held in Moscow from 11 to 14 April. The symposium was dedicated to Academician N. N. Semenov on the occasion of his 70th birthday and 50th year of scientific activity. Semenov himself made the opening address to some 500 Soviet and foreign scientists by outlining the history of development of his theory of chain reactions and combustion processes and by discussing the theory of branched chain reactions, including the latest developments which have resulted from experimental work at the Institute of Chemical Physics, AS USSR. A significant new contribution to the theory of branching was made when Semenov introduced the idea that molecules in the excited state participate in branching. Semenov also advanced a hypothesis of the exciton mechanism to explain low-temperature polymerization in the solid phase without activation energy.

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ACC NR: AP6021960

In addition to others branched chain reactions in the gas phase were treated in several papers: Nalbandyan, A. B. (Institute of Chemical Physics, AS USSR), and Voyevodskiy, V. V., and V. N. Panfilova (Institute of Chemical Kinetics and Combustion, AS USSR, Siberian Department) -- rarefied flame reactions of sulfur and sulfur compounds, and hydrogen with hydrocarbon additives, respectively; Sabo, Z. (Institute of Inorganic and Analytical Chemistry, Hungarian AS) -- decomposition reactions.

Liquid phase reactions were discussed in a series of papers, the most interesting of which were: Emanuel, N. M. (Institute of Chemical Physics, AS USSR) -- oxidation of organic compounds, specifically mild oxidation of low-molecular weight compounds under pressure and co-oxidation of aldehydes and olefins, which yields large quantities of epoxy compounds; Neyman, M. B., Yu. A. Shlyapnikov, V. B. Miller, and V. S. Pudov (Institute of Chemical Physics, AS USSR) -- oxidation inhibiting activity of biphenols with narrow-spaced active groups; Roginskiy, S. Z., Andrianov, T. I., and Yu. N. Rufov (Institute of Chemical Physics, AS USSR) -- the role of oxygen-free radicals in hydroperoxide formation and the discovery of new solid catalysts and inhibitors of this process; Yenikolopyan, N. S. (Institute of Chemical Physics, AS USSR) the chain-transfer with breaking mechanism of the formation of heterochain polymers by ionic polymerization; and Dolgoplosk, B. A. (Institute of Petrochemical Synthesis in A. V. Topchiyev, AS USSR) -- stereo-specific polymerization of diene specifically polybutadiene via π -allyl and π -crotyl complexes of transition metals.

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ACC NR: AP6021960

Free-radical reactions were studied, in addition to others, in the papers by: Kondrat'yev, V. N., Academician -- review of the state-of-the-art of research with emphasis on kinetic measurements of elementary free-radical reactions, specifically of thermal generation, exchange, and recombination reactions; Azatyán, V. V., and Dodonov, A. F., G. K. Lavrovskaya and V. L. Tal'roze (Institute of Chemical Physics, AS USSR) -- determination of rate constants of the reactions of atomic hydrogen, oxygen, and hydroxyl radicals and of atomic hydrogen with ethylene molecules, respectively; Shlyapnikova, N. L., A. P. Ballod, and V. Ya. Shtern -- detection of CH_2NO_2 , CH_2O , CH_3O radical CH_3ONO , and CH_3ONO_2 in products of the

reaction of methyl radicals with nitrogen dioxide; Bagdasar'yan, Kh. S. (Karpov Physicochemical Institute) -- the problem of reactivity of free radicals; Freydlina, R. Kh (Institute of Heteroorganic Compounds, AS USSR) -- investigation of the free-radical mechanism of telomerization and intramolecular rearrangement of free-radicals; and Razuvayev, G. A., and N. S. Vyazankin (Laboratory of Polymer Stabilization, AS USSR) -- new research data on chain reactions with organometallic compounds, e.g., bis-[triethylgermyl] cadmium with CCl_4 to yield $\text{[(C}_2\text{H}_5)_3\text{Ge}]_2\text{CCl}_2$ at -75°C .
[ATD PRESS: 5030-F]

SUB CODE: 07 / SUBM DATE: none

Card 3/3 af

L 29344-66 EWP(j)/EWT(m) RM

ACC NR: AP6018592

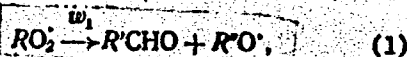
SOURCE CODE: UR/0379/66/002/002/0204/0212

AUTHOR: Zaikov, G. Ye.; Kazancheva, S..D.; Mayzus, Z. K. 23ORG: Institute of Chemical Physics, AN SSSR, Moscow (Institut khimicheskoy fiziki AN SSSR) 8TITLE: Effect of water on the rate and course of oxidation of organic substances

SOURCE: Teoreticheskaya i eksperimental'naya khimiya, v. 2, no. 2, 1966, 204-212

TOPIC TAGS: chemical reaction kinetics, oxidation reaction, reaction rate, methyl ethyl ketone, free radical reaction, oxidation kinetics

ABSTRACT: A study was made of the effect of water as a polar solvent with a high dielectric constant on the kinetics of free radical reactions in the oxidation of polar organic compounds such as methyl ethyl ketone. Earlier, the authors established that a nonpolar solvent (benzene) contributed to an increase in the relative yield of the products of peroxide radical decomposition:



where R' and R'' are radicals containing fewer C atoms than the R radical. A polar solvent like water was expected to have the opposite effect, i.e., to increase the rate of the bimolecular reaction:



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and to simultaneously decrease the rate of the reaction (1). This expectation was confirmed by experimental data which were obtained by chromatographic analysis of the products of methyl ethyl ketone oxidation with air in an autoclave at 160C and 50 atm pressure. Experimental kinetic curves of methyl ethyl ketone consumption and of the accumulation of various oxidation products indicated that the total oxidation rate decreased with an increase in the $C_4H_8O:H_2O$ molar ratio up to 1:20, but that the rate of reaction (1) decreased much faster than that of reaction (2). Total effect of water addition was to increase the rate of accumulation of the products of reaction (2), i.e., of acetic acid, the content of which reached 98—99% of the consumed methyl ethyl ketone at 1:20 dilution. Thus, water may be considered as a selective solvent which secured a practically exclusive formation of one basic product. This method of increasing selectivity of oxidation offers a practical possibility of controlling chemical reactions. A chemical mechanism of formation was proposed for various oxidation products and was used to calculate the rates of all free radical chain reactions involved in the process. The main cause of the increase in selectivity of oxidation was believed to be the relative increase in the rate of reaction (2), owing to the high polarity of water. Orig. art. has: 4 figures, 3 tables, and 11 formulas. [JK]

SUB CODE: 07/ SUBM DATE: 20Jul65/ ORIG REF: 016/ OTH REF: 007/ ATD PRESS:

5009

Cord 2/2 CC

L 43750-66 EWT(m)/EWP(j) JW/RA/JWD

ACC NR: AP6030451

SOURCE CODE: UR/0204/66/006/004/0603/0607

AUTHOR: Karpukhina, G. V.; Mayzus, Z. K.; Matiyenko, L. I. 52
46

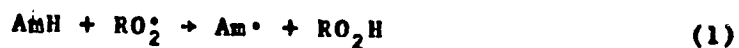
ORG: Institute of Chemical Physics, AN SSSR (Institut khimicheskoye fiziki AN SSSR)

TITLE: Interaction of phenol and aromatic-amine inhibitors in hydrocarbon-oxidation reactions

SOURCE: Neftekhimiya, v. 6, no. 4, 1966, 603-607

TOPIC TAGS: oxidation inhibition, antioxidant additive, combustion modifier, synergism, *ALKYLPHENOL*, *FREE RADICAL STABILIZATION*

ABSTRACT: A relationship has been established between the occurrence of synergism between two oxidation inhibitors—an aromatic amine (AmH) and an alkylphenol (PhOH)—and the structure of the alkylphenol. This synergism is assumed to be due to a free-radical reaction of the two inhibitors:



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The effect of phenols having different substituents ortho or para to the OH group, in conjunction with N-phenyl- β -naphthylamine (Neozone D) was studied in the azobisisobutyronitrile-initiated low-temperature (60--70C) oxidation of ethylbenzene, by a chemiluminescence technique and by chemical analysis. It was shown that the synergism occurs in the case of o,o'-dialkylphenols but not in the case of o-alkyl and nonsubstituted phenols. This was attributed to the fact that the rate of amine regeneration (reaction (2)) increases with increasing PhO[•] radical stability, which in turn increases with increasing steric hindrance of the phenol's OH group. A relationship was also established between the inhibitor effectiveness of the phenols [in the absence of the amine] and their structure. The criterion of inhibitor effectiveness used was the constant of the reaction of the phenol with RO₂ radicals. The activation energy of the reaction of 2,4,6-tri-tert-butylphenol with RO₂ radicals was found to be 3.4 kcal/mol. The authors thank N. M. Emanuel, A. A. Berlin, and V. V. Yershov for discussing this study. Orig. art. has: 4 figures. [SM]

SUB CODE: 07, 11, 21/ SUBM DATE: 02Jul65/ ORIG REF: 005/ OTH REF: 003
ATD PRESS: 5076

Card 2/2 M/S

1, 25357-66 EWT(m)/ETC(f)/EWG(m)/EWP(j)/T/ETC(m)-6 DS/JD/WW/HW/RM

ACC NR: AP5013383

SOURCE CODE: UR/0195/66/007/002/0332/0335

AUTHOR: Bulgakova, G. M.; Mayzus, Z. K.; Skibida, I. P.ORG: Institute of Chemical Physics, AN SSSR (Institut khimicheskoy fiziki AN SSSR)TITLE: Mechanism of chain branching during catalyzed oxidation of n-decane in the presence of cobalt stearate

SOURCE: Kinetika i kataliz, v. 7, no. 2, 1966, 332-335

TOPIC TAGS: decane, cobalt compound, catalysis, hydroperoxide, free radical

ABSTRACT: The catalyzed decomposition of n-decyl hydroperoxide (ROOH) in a nitrogen atmosphere was studied at 60°-100°C in order to determine the mechanism of chain branching during the catalytic oxidation of n-decane with cobalt stearate CoSt_2 as the catalyst. The chain branching rate W was found to increase with the hydroperoxide concentration up to a certain value $[\text{ROOH}] = [\text{ROOH}]_{\text{max}}$ above which the rate of consumption of the hydroperoxide remains constant, indicating that the formation of radicals (produced by the decomposition of the hydroperoxide) is preceded by the formation of a complex. Kinetic data showed that the complex had the composition $[\text{St}_2\text{Co}\cdot\text{ROOH}]$. The rate constant of the formation of radicals as a result of the reaction of this complex with cobalt stearate was calculated to be $k_3 = 2 \cdot 10^{17} \exp(-24500/RT)$ l/mol sec,

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and the equilibrium constant for the formation of the complex $K = 6 \cdot 10^{-5} \exp(1000/RT)$ l/mol. The results indicate that the great effectiveness of cobalt salts as a catalysts is due to the high value of the rate constant of decomposition of the hydroperoxide into radicals, which is almost 10^3 times greater than the rate constant of radical decomposition in the absence of catalyst. Orig. art. has: 3 figures, 10 formulas.

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OTH REF: 003

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