Emanuel, N. M

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.
Catalysis, B-9

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 411

Author: Vasil'yev, R. F., and Emanuel, N. M.

Institution: Academy of Sciences USSR

Title: Kinetics of the Oxidation of Acetaldehyde by Acetyl Hydroperoxide

Original Periodical: Izv. AN SSSR, section on chemical sciences, 1956, No 4, 387-396

Abstract: Two possible mechanisms are discussed for the reactions: $CH_3-CHO + CH_3COOOH \rightleftharpoons Y \rightarrow 2CH_3COOH$ (1) and $CH_3CHO + CH_3COOOH \rightleftharpoons Y$; and $CH_3CHO + CH_3COOCH \rightleftharpoons 2CH_3COOH$ (Y is the peroxide product formed during the reaction). The kinetics of the disappearance of CH_3COOOH and the accumulation of CH_3COOH have been investigated in toluol solutions at 18-40° and are adequately described by the step mechanism (1); in particular, the rate of formation of the acid shows an initial increase. Thus, Y appears to be an intermediate and not a side-product of the reaction. The value $1.6 \cdot 10^3 \exp(-5{,}500/RT)$ mol/liter

Card 1/2

Emanuel, N. M.

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.
Catalysis, B-9

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 412

Author: Vasil'yev, R. F., Terenin, A. N., and Emanuel, N. M.

Institution: Academy of Sciences USSR

Title: Spectroscopic Investigation of the Intermediate Product and the Transition Step in the Oxidation of Acetaldehyde by Acetyl Hydroperoxide

Original Periodical: Izv. AN SSSR, section on chemical sciences, 1956, No 4, 397-402

Abstract: The intermediate peroxide product (I) formed during the reaction of CH_3COOOH (II) with CH_3CHO (III) (see preceding abstract) has been crystallized from toluene solution at -50° and dissolved in nitromethane. The solution was placed in a cuvette with polyethylene windows, and its spectrum recorded with an IR spectrophotometer. In the spectrum the average intensity band 847 cm^{-1}, produced by the valency oscillations of the -0-0- group, was found. From the 847 band and the 586 (II) and 947 cm^{-1} (III) bands in the temperature range

Card 1/2

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.
Catalysis, B-9

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 412

Abstract: -20 to 20°, the kinetics for the establishment of the equilibrium II + III $\rightleftarrows$ I were studied qualitatively as well as the kinetics for the formation of acetic acid. The small shift in the 847 band of I relative to the II band (856 cm^{-1} indicates that I apparently has a hydroperoxide structure, e.g., $CH_3CH(OOH)OC(O)-CH_3$.

Card 2/2

Emanuel, N. M.

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.
Catalysis, B-9

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 413

Author: Vasil'yev, R. F., Terenin, A. N., and Emanuel, N. M.

Institution: Academy of Sciences USSR

Title: The Effect of the Solvent on the Rate of Oxidation of Acetaldehyde by Acetyl Hydroperoxide from the Point of View of Hydrogen-Bonding

Original Periodical: Izv. AN SSSR, section on chemical sciences, 1956, No 4, 403-407

Abstract: The rate for the first step of the reaction (see preceding abstract) at 24.2° is the same in $CHCl_3$, $C_6H_5CH_3$, C_6H_6, and C_6H_5-NO_2; the rate is somewhat higher in CCl_4 and considerably lower in CH_3OH, CH_3NO_2 and CH_3COCH_3. In the IR absorption spectra of CH_3COOOH solutions in CH_3NO_2 and CH_3COCH_3 there are observed, in addition to the bands due to intermolecular hydrogen bonding in CH_3COOOH (3,310 cm^{-1}), broad bands with maxima at 3,385 and 3,285 cm^{-1}, which are ascribed to intramolecular hydrogen bonding (MVC /mezmolekulyarnyy vodorodniy svyazi/)

Card 1/2

USSR/Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry.
Catalysis, B-9

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 413

Abstract: between the solvent and CH_3COOOH. In the spectrum of the solution of CH_3COOOH in $C_6H_5NO_2$ there are observed only the 3,310 cm^{-1} bands: MVC is either absent or very weak. At the same time it can be assumed that MVC takes place in the system $CH_3COOOH + CH_3OH$. In the remaining solutions MVC is not possible. The authors are of the opinion that the inhibition of the reaction observed in a number of solvents is due to the hindering effect of the molecules which are joined to the CH_3COOOH by hydrogen bonds.

Card 2/2

Emanuel', N. M.

B-9

USSR/Physical Chemistry - Kinetics. Combustion.
Explosives. Topochemistry. Catalysis

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 3784

Author : Sedova M.F., Emanuel' N.M.
Inst : Department of Chemical Sciences, Academy of Sciences USSR
Title : Kinetics of Ethane Oxidation in the Presence of Hydrogen Bromide.

Orig Pub : Izv. AN SSSR, Otd. khim. n., 1956, No 6, 658-667

Abstract : Kinetics of oxidation of C_2H_6 in the presence of HBr was studied at 205-245°, pressure of 100-200 mm Hg, and different proportions of C_2H_6, O_2 and Hbr. The main product of the reaction is CH_3COOH, and its formation ceases long before expenditure of the starting materials. Yield of CH_3COOH increases with increasing concentration of HBr, up to 15%, and remains constant (~40% of the initial C_2H_6) on further increase of HBr concentration. Energy of activation of CH_3COOH formation is 23 Kcal/mole.

Card 1/2

Emanuel, N. M.

Category: USSR B-9

Abs Jour: Zh--Kh, No 3, 1957, 7547

Author : Blyumberg, E. A., Pomanskiy, A. N., and Emanuel, N. M.
Inst : Academy of Sciences USSR
Title : Concentration Limits for Flame Propagation in Mixtures of Hydrogen and Oxides of Nitrogen

Orig Pub: Izv. AN SSSR, Section on Chemical Sciences, 1956, No 7, 764-770

Abstract: The region of flame propagation in mixtures of H_2 and oxides of N_2 and N_2 has been determined and is presented graphically; the mixtures were ignited by a spark. The lower concentration limit (percent H_2, first number) and the amount of N_2 (percent in mixture) required to render the mixture completely insensitive were found to be as follows: for N_2O, 5.0, 86.0, 75.0; for NO, 11.4, 60.0, 40.0; for an equilibrium mixture $2NO_2 \rightleftarrows N_2O_4$, 24.0, 87.6, 60.0. The region of flame propagation in mixtures of H_2-N_20-NO has also been determined.

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EMANUEL, N. M.

USSR/ Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry. Catalysis B-9

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11229

Author : Vartanyan L.S., Knorre D.G., Mayzus Z.K., Emanuel' N.M.

Title : Kinetic Characteristics of n-Decane Oxidation Following the Initial Macroscopic Stage of Catalyst Transformation

Orig Pub : Zh. fiz. khimii, 1956, 30, No 3, 665-675 (English summary)

Abstract : Co stearate and Mn laurate which catalyze oxidation of n-decane at 140°, undergo in the course of the reaction a cycle of valency transformations which terminates by a separation of the catalyst into the precipitate (RZhKhim, 1955, 36911; 1956, 35357). Removal of catalyst precipitate (CP) does not affect the kinetics of accumulation of alcohols, carbonyl compounds, acids and esters. Concentration of peroxide increases after removal of CP to a value characteristic of non-catalyzed oxidation. It is shown by calculations that the results obtained can not explained in the scope of the generally accepted chain scheme of oxidation of hydrocarbons, since this scheme assumes that rate of accumulation of final oxidation products, after removal of CP, should decrease, and kinetic

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USSR/ Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry, Catalysis B-9

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11229

curves approach the curves of non-catalyzed oxidation. The authors consider that during the initial macroscopic stage of catalyst transformation there are formed metal-free intermediate compounds which ensure progress of the process at a rate characteristic of catalyzed oxidation, also after removal of CP.

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EMANUEL, N.M.

USSR/Physical Chemistry, Kinetics, Combustion, Explosions, Topochemistry, Catalysis. B-9

Abs Jour : Ref Zhur - Khimiya, No 7, 1957, 22396.

Author : N. M. Emanuel'.
Inst : Not given
Title : Liquid Hydrocarbons Oxidation, initiated by Gaseous Catalizers in the Original Period of Process Development.

Orig Pub : Zh. fiz khimii, 1956, 30, No 4, 847-855.

Abstract : An important consequence of N. N. Semenov's theory of chain reaction with degenerated ramification is stressed. This consequence consists in a possibility of efficient conduct of such reactions after only a short stimulating action on the process in its initial stage of development. The method proposed by the author earlier (R. Zh. Khim 1956, 50223) of original gaseous initiation of chain-reactions of hydrocarbon oxidation in liquid phase is applied to reactions of n- hexadecane (I) and paraffine initiated by NO_2. The rate of formation of carbonyl compounds and acids by I oxidation at 127° increases rapidly upon additions of O_2 which is incoming for oxidation and 10% of NO_2 during the first 10 minutes of the re-

Card 1/2

USSR/Physical Chemistry, Kinetics, Combustion, Explosions, Topochemistry, Catalysis. B-9

Abs Jour : Ref Zhur - Khimiya, No 7, 1957, 22396.

action. Further oxidation is conducted by pure O_2. Similarly initiated oxidation of the "Kepsen" brand of paraffine produces an acid number of 70 mg in 24 hours, whereas without NO_2 the reaction doesnot even begin within 370 hours.

Card 2/2

EMANUEL, N. M.

USSR/ Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry. Catalysis B-9

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11231

Author : Vartanyan L.S., Mayzus Z.K., Emanuel' N.M.
Title : Kinetic Characteristic of Hydroperoxides as Intermediate Products of the Reaction of Oxidation of n-Decane

Orig Pub : Zh. fiz. khimii, 1956, 30, No 4, 856-861

Abstract : Decomposition of hydroperoxide formed on oxidation of n-decane (I) at 120-140° was studied in a medium of I, oxidized to different extent. The reaction in of 1-st order and values of velocity constant decrease with increasing extent of oxidation of I. Energy of activation of hydroperoxide decomposition, with a constant extent of oxidation, is 24 kcal/mole. Comparison of summative kinetic curve of the rate of formation of final reaction products (alcohols, carbonyl compounds, acids and esters) with kinetic curve of hydroperoxide decomposition rate, shows that the main portion of final oxidation products (~80%) is formed as a result of decomposition of intermediate hydroperoxide.

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EMANUEL, N. M.

USSR/ Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry. Catalysis

B-9

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11230

Author : Vartanyan L.S., Mayzus Z.K., Emanuel' N.M.

Title : On Sequence of Formation of Oxidation Products of n-Decane

Orig Pub : Zh. fiz. khimii, 1956, 30, No 4, 862-870

Abstract : To determine the sequence of formation of oxidation products of n-decane use was made of the kinetic procedure of removing from the reaction mixture (at a certain moment of the reaction) the intermediate product of oxidation -- the hydroperoxide(I). Study of the subsequent kinetics of accumulation of the final reaction products shows that removal of peroxides affects mostly the kinetics of formation of alcohols, to a lesser extent the kinetics of carbonyl compounds, and has pratically no effect on kinetics of accumulation of the acids. Products of decomposition of I, formed on oxidation of decane, are alcohols and carbonyl compounds. Acids are not formed directly on decomposition of I. The results obtained indicate the following sequence in the formation of products:

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USSR/ Physical Chemistry - Kinetics. Combustion. Explosives. Topochemistry. Catalysis B-9

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11230

$$\begin{tikzcd}
& \text{alcohols} \arrow[dd] & \\
\text{I} \arrow[ur] \arrow[dr] & & \\
& \text{ketones} \arrow[r] & \text{acids.}
\end{tikzcd}$$

Mathematical analysis of the form of kinetic curves of oxidation product accumulation after removal of peroxides, yields in the case of such a sequence, results that coincide with experimental data.

2/2

Emanuel, N.M.

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topochemistry, Catalysis.

B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3855.

Author : Ye. T. Denisov, N.M. Emanuel'.
Inst : Moscow State University.
Title : Mechanism of Catalysis by Cobalt Srearate at Initial Period of Cyclohexane Oxidation.

Orig Pub: Zh. fiz. khimii, 1956, 30, No 11, 2499 - 2509.

reaction catalyzed

USSR/Physical Chemistry - Kinetics, Combustion, Explosions, Topochemistry, Catalysis. B-9

Abs Jour: Referat. Zhurnal Khimiya, No 2, 1958, 3855.

of the initial stage products; additions of cyclohexanol (3.35 m-mole per lit) increase the duration of the retarded reaction. If St_2Co containing crystallization water was added to I, the transition of Co^{2+} into Co^{3+} and the initiation of the oxidation process do not take place. The authors think that in the initial oxidation period a rapidly retarded macroscopic initiating stage takes place, in which stage Co^{2+} converts into Co^{3+} and the latter catalyzes the further process course. Experiments with different St_2O concentrations and with additions of Co^{2+} to the developed reaction indicate that Co^{2+} retards the reaction. In the opinion of the authors, initiating is not connected with the reaction between St_2O and peroxide, but it occurs with the participation of the St_2CoO_2 complex with I.

Card : 2/2 -8-

<u>EMANUEL, N. M.,</u> NEYMAN, M. B., NALBANDYAN, A. B.

"Employing the method of labelled atoms in studying the successive stages of hydrocarbon oxidation," a paper submitted at the International Conference on Radioisotopes in Scientific Research, Paris, 9-20 Sep 57.

EMANUEL, N.M.

PHASE I BOOK EXPLOITATION 439

Semenov, Nikolay Nikolayevich

O tsepnykh reaktsiyakh i teorii goreniya (Chain Reactions and the Theory of Combustion) Moscow, Izdatel'stvo "Znaniye," Series 8, Nr 17, 1957. 31 p. 46,500 copies printed.

Ed.: Faynboym, I. B.; Tech. Ed.: Gubin, M. I.; Corrector: Bauer, G. M.

PURPOSE: The pamphlet publicizes N. N. Semenov's paper read at the Nobel Prize presentation ceremony in Stockholm, 1956.

COVERAGE: This paper reviews progress in the study of chain reactions. Research was divided into two groups 1) application of chemical kinetics to the theory of combustion and detonation, and 2) study of the mechanism of chemical reactions, in particular, chain reactions. The author points out the great contribution of Soviet scientists to the development of chain-reaction concepts, to the theory of thermal detonation, and to the general theory of combustion. The paper covers Western as well as Soviet achievements. The second part of the pamphlet is a biography of Nikolay Nikolayevich Semenov written by Prof. N. M. Emanuel'. Semenov's contribution to the theory of chain reactions is the main theme.

Card 1/2

EMMANUEL', N.M.

AUTHORS:	Kruglyakova, K. Ye., and Emanuel', N. M.	62-1-2/21

TITLE: Kinetic Characteristics of the Reaction of Propane Oxidation with Oxygen with Chlorine Admixtures in Quartz Crystal Vessels (Kineticheskiye kharakteristiki reaktsii okisleniya propana kislorodom s dobavkami khlora v kvartsevykh sosudakh)

PERIODICAL: Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1957, No. 1, pp. 18-28 (U.S.S.R.)

ABSTRACT: Investigations were conducted to determine the effect of chlorine admixtures in oxygen used for the oxidation of propane at various atmospheric pressures and temperatures ranging from 250 to 355°. It was found that small additions of Cl accelerate the propane oxidation process and increase the yield of oxygen-containing compounds. An increase in temperature from 25C to 355° is followed by a noticeable increase in the amount of peroxides in the oxidation products and the time needed for maximum concentration of the peroxides

Card 1/3

62-1-2/21

Kinetic Characteristics of the Reaction of Propane Oxidation with Oxygen with Chlorine Admixtures in Quartz Crystal Vessels

decreases. The introduction of larger Cl-additions was found to be impractical because it does not increase the yield of valuable oxygenous products and the deep-burning processes are stimulated. The total amount of carbonyl compounds was determined by the ordinary hydroxylamine method and it is shown that the error in determining the carbonyl compounds, due to the presence of peroxides which also react with the hydrochloride of the hydroxylamine, was no higher than 3 - 5% of their total content. The content of acetaldehyde, formaldehyde, organic acids and peroxides reaches its maximum within 1 min. The peroxide, being an intermediate molecular product, is being slowly consumed, whereas the acetaldehyde, formaldehyde and organic acids remain unchanged during the continuing oxidation process. The gaseous reaction products include: CO_2, Co, and unsaturated hydrocarbons. The nature of the peroxides forming during Cl- catalyzed oxidation of propane is described as a mixture of hydrogen peroxide of isopropyl and hydrogen peroxide.

Card 2/3 Graphs, drawing. There are 9 references, of which 7 are Slavic.

62-1-2/21

Kinetic Characteristics of the Reaction of Propane Oxidation with Oxygen with Chlorine Admixtures in Quartz Crystal Vessels

ASSOCIATION: Academy of Sciences USSR, Institute of Chemical Physics

PRESENTED BY:

SUBMITTED: June 8, 1956

AVAILABLE: Library of Congress

Card 3/3

AUTHOR: EMANUEL, N.M. PA - 2198
TITLE: The chemical chain reactions and the processes of combustion and
explosions.(In connection with the awarding of the Nobel Price to
PERIODICAL: Atomnaia Energiia, 1957, Vol 2, Nr 1, pp 61 - 65 N.N.SEMENOV.
Received: 3 / 1957 Reviewed: 4 / 1957.

ABSTRACT: N.N.SEMENOV's discovery of branched chemical chain reactions (especially the chainlike inflammation), his general theory of chain reactions, his theory of thermal reactions, and the determination of the connections between combustion, explosion, flame propagation, and the laws for the process of combustion soon found world-wide acknowledgement. For the investigation and the development of SEMENOV's new ideas the Institute for Chemical Physics of the Academy of Science of the U.S.S.R. was established in 1931. The laboratories of this institute carried out many fundamental investigations on chain reactions, processes of combustion, and explosions. N.N.SEMENOV carefully investigated long before the discovery of the chain mechanism of the fission of uranium and plutonium nuclei, the mechanism of the chainlike ramifications at chemical reactions. In 1926 SEMENEV and his colleagues detected in the Laboratory for Electronic phenomena of the Leningrad Physical-Technical Institute, that during the influx of oxyde into a container filled with phosphorus vapor phosphorescence does not occur at once but only after reaching a certain "critical" pressure of oxyde. This threshold of the pressure also depends on the diameter

Card 1/2

The chemical chain reactions and the processes of combustion and explosions. PA 2198

of the reactor. Besides, the reaction in systems with dimensions which are smaller than certain "critical" dimensions cannot accelerate by itself to an explosion. SEMENOV explained this behavior with chains of chemical reactions. The notion "critical diameter" in the case of chainlike chemical reactions fully corresponds to the notion of the "critical dimension of the reactor" in nuclear physics. In this theory the idea on the breaking off of the chain on the walls of the reactive container and inside the reacting mixture was formed. The loss of free atoms and radicals which causes the breaking off of the chemical reaction chain is completely analogous to the losses of neutrons during nuclear chain reactions. These numerous investigations of the Institute for Chemical Physics prove the frequent occurence of chain reactions in chemistry. SEMENOV proved the general theories of chain reactions very thoroughly by experiments. Besides, he set up a theory for the interaction of chains. In conclusion some examples and applications are discussed.

Card 2/2

ASSOCIATION: Not given
PRESENTED BY:
SUBMITTED:
AVAILABLE: Library of Congress.

EMANUEL' N.M,

KNORRE, D.G.; LYASKOVSKAYA, Yu.N.; EMANUEL', N.M.

Oxidation kinetics of fats. Izv. AN SSSR Otd. khim. nauk no.6:678-683 Je '57.
(MIRA 10:11)

1. Institut khimicheskoy fiziki AN SSSR i Vsesoyuznyy nauchno-issledovatel'skiy institut myasnoy promyshlennosti.
(Oils and fats) (Oxidation)

Emanuel, N.M.

BLUMBERG, Ye.A.; VASIL'YEV, V.I.; EMANUEL', N.M.

Effect of hydrocarbon additions on the concentration limits of flame spreading in gas mixtures containing hydrogen. Izv. AN SSSR. Otd. khim. nauk no.10:1172-1180 O '57. (MIRA 11:3)

1. Institut khimicheskoy fiziki AN SSSR.

(Combustion) (Hydrocarbons) (Inhibition (Chemistry))

EMANUEL', N.M.

62-11-3/29

AUTHOR: Emanuel', N. M.

TITLE: New Problems in the Field of Chain Reactions (Novyye problemy v oblasti tsepnykh reaktsiy).

PERIODICAL: Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk, 1957, Nr 11, pp. 1298-1313 (USSR)

ABSTRACT: The following can be said based on the survey given here. Many properties and particularities of a branched chain process can serve as fundament for elaboration of new principles for the controlled execution of the oxydation processes of hydrocarbons. The capacity of the degenerated branched chain reaction in the oxydation of hydrocarbons in liquid phase for self-maintaining and self-accelerating development offers the possibility to stimulate these reactions by means of influence for a short time of gas-initiators, penetrating rays, salt-catalysts and the like in the initial phase of the process development ("taking away" the induction period). In homogenous catalysis (induction) of the oxydation processes of hydrocarbons the phenomena of a reaction process are distributed according to phases, in the form of successive, chronologically

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New Problems in the Field of Chain Reactions. 62-11-3/29

separated, macroscopic phases. In some cases an analogical process according to phases also becomes manifest in non-catalyzed oxydation. Additions of negative catalysts (inhibitors) can have a different effect on the development of these phases. In connection with this high differences in the mode of action of the inhibitors can occur when introducing them into the initial and the reacting mixture. The presence of chronologically separated macroscopic phases permits to direct the oxydation processes by modification of the conditions after the reaction process, with transition from one macroscopic phase to the next. There are 12 figures.

ASSOCIATION: Institute for Chemical Physics of the AN USSR (Institut khimicheskoy fiziki Akademiii nauk SSSR).

SUBMITTED: September 17, 1957.

AVAILABLE: Library of Congress

Card 2/2

EMANUEL', N.M., professor.

Nobel prize winner Academician Nikolai Nikolaevich Semenov.
Vest.Mosk.un. 12 no.1:182-187 '57. (MLRA 10:8)
(Semenov, Nikolai Nikolaevich, 1893-)

EMANUEL, N.M.

PA - 2618

AUTHOR: EMANUEL, M.N.

TITLE: Contribution of the Development of Chemical Physics. On the Occasion of the 25th Anniversary of the Existence of the Institute for Chemical Physics of the Academy of Science of the U.S?S.R. (Vklad v razvitiye khimicheskoy fiziki. K 25-letiyu Instituta khimicheskoy fiziki Akademii Nauk SSSR, Russian)

PERIODICAL: Vestnik Akademii Nauk SSSR, 1957, Vol 27, Nr 3, pp 69 - 81 (USSR)

Received: 5 / 1957 Reviewed: 6 / 1957

ABSTRACT: In his article the author mentions the revolutionizing effect produced by the progress recently made in physics in various fields. The work performed by the above Institute is described as consisting in "making physics the basis of socialist industry and technical engineering in the U.S.S.R.". The institute began work at Leningrad in 1921 as an independent State institution under the name "Leningrad State Physicsl-Technical Radiological Institute (GFTRI - Gosudarstvyennyy fiziko-technicheskiy ryentgyenovskiy Institut) under the management of A.F.Ioffe, member of the Academy. The laboratory for electron chemistry, which was established at that time under the management of N.N.Syemyenov, is described as the most important department of that Institute. A short outline of the history and of the achievements of the institute (1921 - 1956) is given. It was incorporated in the Academy of Science in 1939. The first work carried out under the supervision

Card 1/3

PA - 2618

Contribution to the Deveopment of Chemical Physics.

of N.N.Syemyenov concerned the investigation of electric fields, the analysis of electric breakdown in the vacuum and in gases. Later, the heat theory of combustion, and explosion processes was developed and research work was carried out in the fields of condensation, adsorption, polemerization, and colloidal chemistry. In the period of 1925 - 1928 important discoveries were made under Syemyenov with respect to combustion of phosphorus gases under pressure, and the theories of "critical pressure", "chain explosions", and the general theory of combustion processes were developed. The work performed by the Institute in 1931 is described as particularly important because it was at that period that the Institute gained a leading position in world science by its scientific research work in the field of chain reactions. In 1934 N.N. Syemyenov published a monography on "chain reactions" which attained world fame. It was followed by the monography on "Some problems of chemical kinetics and some properties of reaction", in which N.N.Syemyenov mainly dealt with the investigation of the mechanism of chemical reactions, for which he was awarded the Nobel Prize in 1956. Following a suggestion made by N.N.Syemyenov the first research work in the field of nuclear physics, the formation and adsorption of neutrons, the metastability of the excited

Card 2/3

PA - 2618

Contribution of the Deveopment of Chemical Physics.

nucleus, etc were begun in the U.S.S.R. The Institute is continually being extended, particularly by soliciting the services of the most talented scientists of the country, and is expected to make a great contribution towards " enhancing the glory and the power of the U.S.S.R.".

ASSOCIATION: Not given
PRESENTED BY/
SUBMITTED:
AVAILABLE: Library of Congress

Card 3/3

EMANUEL', N.M., professor.

Important contribution to world science; award of the Nobel Prize to Academician N.N.Semenov. Priroda 46 no.2:43-48 F '57.

(MLRA 10:3)

1. Institut khimicheskoy fiziki Akademii nauk SSSR (Moskva)
(Semenov, Nikolai Nikolaevich, 1893)

EMANUEL', N.M., professor.

Outstanding studies on the mechanism of chemical reactions. Priroda 46 no.3:44-48 Mr '57. (MLRA 10:3)

1. Institut khimicheskoy fiziki Akademii nauk SSSR (Moskva).
(Hinshelwood, Cyril, 1897-)

EMANUEL', N. M.

KNORRE, D.G.; MAYZUS, Z.K.; EMANUEL', N.M.

Activation energy of the elementary reaction $RO_2 + RH$ in the oxidation of n-decane. Dokl. AN SSSR 112 no.3:457-460 Ja '57. (MLRA 10:4)

1. Predstavleno akademikom V.N. Kondrat'yevym.
(Chemical reaction--Mechanism)
(Decane)

Emanuel', N.M.

20-3-28/52

AUTHORS: Emanuel', N. M., Denisov, Ye. T.

TITLE: Theoretical Possibility of Oxidation of Benzene to Phenol in the Liquid Phase (O printsipial'noy vozmozhnosti zhidkofaznogo okisleniya benzola v fenol)

PERIODICAL: Doklady AN SSSR, 1957, Vol. 117, Nr 3, pp. 458 - 461 (USSR)

ABSTRACT: The authors here endeavor to determine the oxidation of benzene at temperatures of from 230 - 270° and at a pressure of 50 atmospheres Experiments were carried out in an autoclave device for the oxidation of hydrocarbons in the liquid phase under pressure. At each experiment 200 mm of benzene were introduced into the reactor. Oxidation was carried out by the oxygen of a nitrogen oxygen mixture with the composition 1 : 1. During this process samples were taken of oxidized benzene and were analyzed with respect to their phenol content. With a photocalorimeter also the optical density of the oxidized benzene was measured. At 250° oxidation of the benzene in the liquid phase takes place with noticeable rapidity. With the oxidation of benzene phenol and resins are produced. The kinetic curve of the accumulation of phenol is of S-like character. However, the maximum concentration of phenol in this process amounts to only 0,16 mol percent. In the oxidation of benzene with cobalt

Card 1/3

20-3-28/52

Theoretical Possibility of Oxidation of Benzene to Phenol in the Liquid Phase

stearate this catalyzer directs the reaction into the direction of the condensation of benzene with the production of soot; only small quantities of phenol are produced on this occasion. Small quantities of easily oxidizable substances such as cyclohexane and cyclohexanon accelerate the oxidation of benzene. The corresponding kinetic curves are given. The experimental data obtained here concerning the oxidation of benzene tend to show that this process is a chain-like degenerated, ramified, self-decelerating reaction. The experimental data agree well with a mechanism, which is described in detail. The present paper proves that, in principle, it is possible to attain the oxidation mentioned in the title at temperatures that are near critical temperature. The principle of gas initiation applied on this occasion furnished the best results. The processes for the removal of the self-slowing-down of the processes will have to be examined. There are 3 figures and 4 references, 3 of which are Slavic.

Card 2/3

Theoretical Possibility of Oxidation of Benzene to Phenol in the Liquid Phase. 20-3-28/52

ASSOCIATION: Institute for Chemical Physics AN USSR
(Institut khimicheskoy fiziki Akademii nauk SSSR)

PRESENTED: May 15, 1957, by N. N. Semenov, Academician

SUBMITTED: May 15, 1957

AVAILABLE: Library of Congress

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EMANUEL, N.M.

The Chemical Society of the GDR held its annual meeting 28 Oct.-1 Nov. 1958 in Leipzig. The following papers were presented by the USSR delegation

F. Vilesov and A. Terenin - Physics Inst., LGU "Photoelektronische Emission der Oberflaeche von Halbleiterkatalysatoren".

Ye. Shilov and A. Yasnikov - Inst. Organic Chemistry, AS USSR "Über den Mechanismus der Katalytischen Wirkung von Aminosauren in den Reaktionen der Carbonylverbindungen."

A. Shekhter - Inst. Scientific Information, AS USSR "Zur Elektronenmikroskopie heterogener Katalysatoren."

N. M. Emanuel - Inst. Chemical Physics, AS USSR "Homogene Katalyse und Chemische Induktion bei Langsamen Oxydations-Kettenreaktionen."

A. Ye. Braunshteyn - Inst. Biological & Medical Chemistry, AMS USSR "Allgemeine Fragen der biologischen Katalyse im Licht der Wirkungsweise der Pyridoxalenzyme."

F. Vol'kenshteyn - Inst. Physical Chemistry, AS USSR "Zur Elektronentheorie der Chemisorption und Katalyse an Halbleitern."

V. Kazanskiy and V. Voyevodskiy - Inst. Chemical Physics, AS USSR "Über den Mechanismus einiger Katalytischer Reaktionen die am Palladiummetall unter Beteiligung von Wasserstoff verlaufen."

G. K. Boreskov - Karpov Physical-Chemical Inst., Moscow "Wechselwirkung zwischen Katalysator und Reaktionssystem."

A. A. Balandin - AS USSR "Zum Aufbau Einheitstheorie der Katalyse."

SO: Mitteilungsblatt der Chemische Gesellschaft in der DDR, Sonderheft, 1959, Uncl.

EMANUEL, N.M.

The German Academy of Sciences in Berlin (East Germany) held a Research Colloquium at the Inst. of Medicine & Biology in Nov. 1958. Among the Soviet papers presented were

Meyzel, M. "Die Wirkung der ionisierenden Strahlen auf Mikroorganismen."

Emanuel, [N.M.] Inst. Chemical Physics, AS USSR "Über Probleme der Krebsentstehung."

Demikhov, V. P., Head Lab. of Transplantation of Organs, Chair of Operative Surgery, 1st Moscow Medical Inst. "Die Transplantation von Herz, Lungen, Nieren und Anderen Organen der vergleichender Sicht."

SO: Das Deutsche Gesundheitswesen, 24 Sept. 1959, Uncl.

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5(1) 1

AUTHOR: Emanuel', N.M., Corresponding Member, Academy of Sciences, USSR SOV/55-58-5-1/34

TITLE: Chemical Science on the Threshold of new Tasks (Khimicheskaya nauka na poroge novykh zadach)

PERIODICAL: Vestnik Moskovskogo universiteta, Seriya Matematiki, mekhaniki, astronomii, fiziki, khimii, 1958, Nr 5, pp 3 - 6 (USSR)

ABSTRACT: The author writes on the tasks which arise for Soviet chemistry from the resolutions of the 21-th Conference of the Communist Party of the USSR. The chemical production is to be trebled during the following seven years. The production of synthetic substances from by-products of petroleum hauling, particularly the application of hydrocarbon gases to the production of rubber and fertilizers is to be increased extensively. In this connection the scientific council of the Chemical Department of the Moscow University concluded the research of the synthesis and of the properties of the monomer, of the polymer as well as of the highly molecular combinations, the foundation of a laboratory for condensed ("frost-bound") radicals, the enlargement of the laboratories at all, and the increase of the

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Chemical Science on the Threshold of new Tasks SOV/55-58-5-1/34

standard of education of new chemists. For several times the author refers to the theses of N.S. Khrushchev.

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EMANUEL', N. M. (Correspondent-members AS USSR)

"New Investigations in the Field of Chain Reactions."

Lecture to be delivered by Soviet Scientists at the Brussels Exhibition, August 1958. The delivered lectures will be available in English, French, Flemish and German as individual brochures.
(Priroda, 1958, No. 8, p. 116)

SOV-3-58-8-3/26

AUTHOR: Emanue~~l', N.M.~~, Lenin Prize Laureate, **Corresponding Member** of the USSR Academy of Sciences

TITLE: Important Questions of Higher Education in Chemistry (Vazhnyye voprosy vysshego khimicheskogo obrazovaniya)

PERIODICAL: Vestnik vysshey shkoly, 1958, Nr 8, pp 11 - 19 (USSR)

ABSTRACT: During the Soviet regime chemistry has reached a high level, but still does not meet the requirements of the national economy and the chemical industry. In the production of artificial and sythetic fibre, plastics and other synthetic materials, Soviet chemical production is still behind. It is of utmost importance to intensify scientific research and experimental work in this field. The teaching of chemistry does not pay sufficient attention to the up-to-date subjects (petrochemical synthesis; the problems of high molecular compounds; the theory of chemical processes) and the relations between chemistry and physics, biology and medicine. The chemistry faculties should prepare more qualified research chemists. Every chemist should have a command of quantum chemistry and electronic

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Important Questions of Higher Education in Chemistry SOV-3-58-8-3/26

calculating devices. The program of the faculties should also contain subjects such as biochemistry, biophysics and medical chemistry.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet imeni M.V. Lomonosova (Moscow State University imeni M.V. Lomonosov)

Card 2/2

AUTHOR: Emanuel', N.M., Holder of the Lenin Prize, SOV/29-58-10-11/28
Corresponding Member, Academy of Sciences, USSR

TITLE: Scientists Greet the Komsomol !(Uchenyye privetstvuyut komsomol !)Chemistry as Hobby (Lyubite Khimiyu)

PERIODICAL: Tekhnika molodezhi, 1958, Nr 10, pp 12 - 12 (USSR)

ABSTRACT: Among other things the author writes: Within many centuries mankind took the goods from nature which were used in an almost unchanged form. Thanks to the work of several generations of chemists about 300 000 simple and complicated substances - chemical compounds of the inorganic, lifeless matter could be discovered. When scientists, however, started their experiments with the living nature, e.g. organic substances they were faced by unlimited, unexpected and inexhaustible possibilities. More than 3 000 000 chemical compounds are already known. Today chemistry is the most fascinating field of science. Chemistry supplied man with everything he needed in the course of social development and with which he was not supplied by nature. Chemists started to create nature once over. They produced substances which had not been

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Scientists Greet the Komsomol! Chemistry as Hobby SOV/29-58-10-11/28

known before, and those substances had wonderful and strange properties. Chemistry has a great future . Without exaggeration it may be said that the twentieth century is not only the century of atomic power, of electronics and exploration of outer space but just as well the century of chemistry. With full conviction scientists may invite young people to devote themselves to chemistry. "You won't be sorry since you will enter a field of wonderful transformations, a field where man starts to create another nature". That is how the author closes his paper. There is 1 figure.

EMANUEL' N. M.

5(4) SOV/62-58-12-4/22

AUTHORS: Knorre, D. G., Lyaskovskaya, Yu. N., Piul'skaya, V. I., ~~Emanuel', N. M.~~

TITLE: Inhibition of Oxidation Processes of Fats by Ascorbic Esters (Tormozheniye protsessov okisleniya zhirov efirami askorbinovoy kisloty)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 12, pp 1422-1427 (USSR)

ABSTRACT: In the present paper the antioxidation properties of ascorbyl palmitate and of mixtures of ascorbyl palmitate with tert. butyl oxy-anisole in the oxidation of molten lard by means of an accelerated kinetic oxidation method at increased temperature (Ref 3) was investigated. The possibility of substituting palmitic acid in the production of antioxidants by a mixture of n. acids obtained in the oxidation of paraffin was also determined. It was found that ascorbyl palmitate in a mixture with tert. butyl oxy-anisole can effectively maintain the oxidation processes of melted animal fats caused by atmospheric oxygen. The substitution of palmitic acid by a mixture of synthetic fatty acids (fraction C_{14}-C_{16}) does not exercise any

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Inhibition of Oxidation Processes of Fats by Ascorbic Esters SOV/62-58-12-4/22

unfavorable effect on the antioxidation properties of the preparation in the production of ascorbic ester. The efficiency of the mixture of 0.01% tert. butyl oxy-anisole and 0.02% ascorbyl palmitate as an antioxidant of molten animal fats does not depend on temperature. There are 7 figures, 1 table, and 21 references, 2 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics Academy of Sciences USSR) Vsesoyuznyy nauchno-issledovatel'skiy institut myasnoy promyshlennosti MPM i MP SSSR (All Union Scientific Research Institute for Meat Industry MPM and MP USSR)

SUBMITTED: May 22, 1957

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EMANUEL', N.M.

Chemical science on the threshold of new problems. Vest.Mosk.un. Ser.mat.,mekh.,astron.,fiz.,khim. 13 no.5:3-7 '58. (MIRA 12:4)

1. Chlen-korrespondent AN SSSR.
(Chemistry)

AUTHORS: Denisov, Ye.T., Emanuel', N.M. (Moscow) 74-27-4-1/8

TITLE: The Effective Mechanism of the Inhibitors in Chain Reactions of the Liquid Oxidation Phase (Mekhanizm deystviya ingibitorov v tsepnykh reaktsiyakh zhidkofaznogo okisleniya)

PERIODICAL: Uspekhi Khimii, 1958, Vol. 27, Nr 4, pp. 365-402 (USSR)

ABSTRACT: The report begins by dealing with the importance of inhibitors and the research work carried out in this connection during the past decades. Mention is made of the works by Muro and Dyufres (Ref 7) on antioxidation. After the function of inhibitors had, in their general outlines, become known and the chain theory supplied relatively simple formulae for the description of slowing-down effects theoretical interest in inhibitors began to die down. It was only recently that one of the authors of this paper pointed out that in numerous cases oxidation processes have a far more complicated mechanism than that of the slowly growing and ramified chain avalanche. The present survey is devoted to the analysis of the chemical effective mechanism of inhibitors and to the theoretical interpretation of and the particular effect exercised by inhibitors on the basis of the theory of chain reactions with degenerated

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ramifications as developed by Semenov. The report is divided into the following parts: The chain mechanism of the oxidation of hydrocarbons. The "chain-interrupting" chemical effect exercised by inhibitors; on the separation of the H-atom from the molecule of the admixture InH; on the connection of the free radical with the molecule of the admixture Q; the mechanism of the inhibiting effect of phenols; the mechanism of the inhibiting effect of amines. The next chapter deals with the kinetic characteristic of the effect exercised by inhibitors: 1.) The theory of the effect produced by strong inhibitors. 2.) The theory of the effect produced by weak inhibitors. - The following chapter deals with antioxidizers which exercise a retarding effect upon the velocity of degenerated ramification. Mention is made in this connection of the destructive effect exercised by sulfides upon hydroperoxides, of the problem concerning the modification of the kinetic curve of oxidation of hydrocarbon, of the slowing-down effect produced with respect to the oxidation process of alkaline substances and acids. In conclusion the report deals with the joint effect produced by 2 antioxidizers. In this connection the fact is stressed that the joint effect produced by two substances which are able to destroy peroxides can often produce a greater effect than may be assumed on the strength of the rule of additivity. There are 10 figures, 6 tables, and 81 references, 23 of which are Soviet.

1. Chain reactions--Inhibition 2. Oxidation inhibitors--Analysis

EMANUEL', N., doktor khim.nauk; KNORRE, D., kand.khim.nauk; LYASKOVSKAYA, Yu., kand.tekhn.nauk; PIUL'SKAYA, V., inzh.

Improving the stability of animal fats with antioxidants. Mias. ind. SSSR 29 no.2:52-55 '58. (MIRA 11:5)

1.Institut khimicheskoy ifsiki AN SSSR (for Emanuel, Knorre).
2.Vsesoyuznyy nauchno-issledovatel'skiy institut myasnoy promyshlenn promyshlennosti (for Lyaskovskaya, Piul'skaya).
(Oils and fats, Edible--Preservation)
(Antioxidants)

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AUTHORS: Denisov, Ye.T., ~~Emanuel', N. M.~~ SOV/76-32-10-21/39

TITLE: The Liquid Phase Oxidation of Benzene to Phenol at Temperatures Close to the Critical Point (Okisleniye benzola v fenol v zhidkoy faze pri temperaturakh, blizkikh k kriticheskoy)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol 32, Nr 10, pp 2374 - 2382 (USSR)

ABSTRACT: In an earlier paper (Ref 1) it was pointed out that a series of high-temperature oxidations can be carried out in the gas phase at low temperatures, and in the liquid phase. In the present paper the oxidation of liquid benzene is carried out at 230-270° (especially at 250°) and at a pressure of 50 atmospheres absolute pressure. An autoclave serving for the investigation of the kinetics of processes in liquid phase (Ref 5) was used. Benzene oxidizes in the liquid phase rather rapidly at 250°; phenol and resins are formed as reaction products. An addition of 2 mol% cyclohexane causes an acceleration in the process, whereas 1 mol%

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The Liquid Phase Oxidation of Benzene to Phenol at Temperatures Close to the Critical Point SOV/76-32-10-21/39

cyclohexanone shows a still stronger effect. The addition of 0,15 mol% cobalt stereate led to the opposite effect, i.e. a small formation of phenol took place;however, with a large formation of soot. Experiments carried out with gas injections yielded the best results when nitrogen dioxide was used. Nitrobenzene was qualitatively determined among the oxidation products in this case. The interruption of the gas passage leads to a slowing down of the reaction so that a stimulation by nitrogen dioxide should take place throughout the oxidation process. It is assumed that benzene oxidizes also in the liquid phase according to the chain mechanism. The maximum phenol formation depends on the self-impedance of the benzene reaction.The present reaction is considered in relation to the theory of chain reactions by N.N.Semenov (Ref 9), and the experimental data obtained are compared. The self-impedance of the chain reaction is explained by the accumulation of products that inhibit the reaction by an exchange

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The Liquid Phase Oxidation of Benzene to Phenol at Temperatures Close to the Critical Point SOV/76-32-10-21/39

of active radicals against less active ones. According to a scheme the weakly active free radicals react with intermediate products and the maximum concentration of the intermediate products is lower the higher the inhibition by the oxidation products. On the other hand, the final product will be formed at a maximum velocity in the case that the maximum concentration of the intermediate products is obtained. There are 6 figures and 10 references, 8 of which are Soviet.

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

SUBMITTED: May 15, 1957

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20-119-6-37/56

AUTHORS: Emanuel', N. M., Blyumberg, E. A., Ziv, D. M., Pikayeva, V.L.

TITLE: The Initiating Effect of the Radiation of Radon in the Process of the Oxydation of Isodecane (2,7-Dimethyloctane)(Initsiiruyushcheye deystviye izlucheniya radona v protsesse okisleniya izodekana (2,7-dimetiloktana)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 119, Nr 6, pp. 1183 - 1186 (USSR)

ABSTRACT: The application of the radiations of radioactive gases for the initiation of chain reactions can be very effective and this not only in slow chain reactions in the liquid phase. Besides, the application of radioactive gases allows interesting experiments with chain reactions in the gaseous phase. This work uses as test object the oxidation of isodecane (2,7-dimethyloctane) on the action of α-particles of radon. The authors started from the fact that the processes of the oxidation of the hydrocarbons in the liquid phase represent degenerate-branched chain reactions. Therefore such processes can be stimulated only in the initial period in the development of the process. The

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The Initiating Effect of the Radiation of Radon in the 20-119-6-37/56
Process of the Oxidation of Isodecane(2,7-Dimethyloctane)

action of radon radiation leads to the occurring of active particles (free radicals and atoms), i. e. to the increase of the initial velocity of the production of the chains w_0. The experiments were made in a glass device with oxidation cell. The device and the performance of the experiments are illustrated by a figure. 2 diagrams illustrate the curves for the accumulation of the peroxides and acids in the oxidation of isodecane, initiated by α-radiation of radon (and also by the α-and β-radiation of the decay products of Rn). The short stimulating action of the radon radiation is enough for a considerable decrease of the induction period in the production of the hydro-peroxides. Also the maximum yield of the peroxide compounds is increased. The very strong increase of the production velocity of the active centers must lead to a considerable diminution of the induction period, which also experimentally is observed. Still more effective is the action of the α-radiation of Rn upon the reaction velocity after the end of the induction period. The authors thank V. M. Vdovenko for his inter-

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The Initiating Effect of the Radiation of Radon in the Process of the Oxidation of Isodecane (2,7-Dimethyloctane) 20-119-6-37/56

est in this work and V. M. Permyakov and his collaborators for the production of the radon preparations used in this work. There are 3 figures and 3 references, 3 of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics AS USSR); Radiyevyy institut Akademii nauk SSSR (Radium Institute AS USSR)

PRESENTED: December 28, 1957, by V. N. Kondrat'yev, Member, Academy of Sciences, USSR

SUBMITTED: December 25, 1957

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SOV / 2o-12o-1-28/63

AUTHORS: Knorre, D. G., Pikayeva, V. L., Emanuel', N. M.

TITLE: On the Role Played by the Unsteadiness of the Process in the Stimulation of the Degenerated Branched-Chain Reactions in the Liquid Phase (O roli nestatsionarnosti protsessa pri stimulirovanii vyrozhdenno-razvetvlennykh tsepnykh reaktsiy v zhidkoy faze)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 12o, Nr 1, pp. 1o7 - 11o (USSR)

ABSTRACT: In the present paper the kinetics of a chain reaction with degenerated dislocations and quadratic disconnection of the chains are calculated, taking into account the unsteadiness of the process in the initial period of development of the process. The problem of the influence of the duration of initiation on the initial stage of the reaction, mainly on the duration of the induction period, is of basic importance. Therefore the calculation is carried out without taking into account the consumption of the intermediate product which begins to exert influence on the kinetics of the process only in the deeper phases

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On the Role Played by the Unsteadiness of the Process in the Stimulation of the Degenerated Branched-Chain Reactions in the Liquid Phase SOV/ 20-120-1-28/63

of the transformation. It is further shown that the breaking is realized by the recombination of the radicals $RO_2^{\cdot}$, which as a rule takes place at oxygen pressures close to atmospheric pressure. On these conditions the system of equations describing the kinetics of the filling of the intermediate product has the form

$$\frac{d\left[RO_2\right]}{dt} = w_0 + k_p\left[ROOH\right] - k_{recomb}\left[RO_2^{\cdot}\right]^2, \frac{d\left[P\right]}{dt} = k\left[RO_2\right]\left[RH\right].$$

k_{recomb} or k, respectively, denote the constants of the recombination velocity of the radicals $RO_2^{\cdot}$ and of the propagation reaction of the chain: $RO_2^{\cdot} + RH \longrightarrow ROOH + R^{\cdot}$. These differential equations are transformed by the introduction of dimensionless variables, and then are integrated. The discussed calculation was carried out for a model ramification of a paraffin, the isodecane. A diagram shows the kinetic curves of the accumulation of hydrogen peroxide calculated for the cases $k_{recomb}/k = 10^3$ and 10^5, as well as the curves calculated by

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On the Role Played by the Unsteadiness of the SOV/20-120-1-28/63
Process in the Stimulation of the Degenerated Branched-Chain Reactions in the Liquid Phase

using the condition of the quasisteadiness. In either case qualitatively similar results are obtained. The calculation carried out on the condition of the quasisteadiness of the process supplies a completely wrong impression on the intensity of the action of the initiator on the kinetics of the oxidation. The rigorous solution of the system of differential equations for the kinetics of the accumulation of the intermediate product in the reactions of the oxidation of the chains with quadratic breaking makes possible the explanation of the experimentally observed induction periods and promotes the understanding of the effects of the initial stimulation of these processes. There are 3 figures and 11 references, 9 of which are Soviet.

PRESENTED: December 25, 1957, by V.N.Kondrat'yev, Member, Academy of Sciences, USSR
SUBMITTED: December 22, 1957

Card 3/4

AUTHORS: Emanuel', N. M., Lipchina, L. P. SOV/20-121-1-40/55

TITLE: Leucosis in Mice and Some Characteristic Features of Its Development Under the Action of Certain Inhibitors of Oxidizing Chain Processes (Leykoz u myshey i osobennosti yego razvitiya pri vozdeystvii ingibitorov tsepnykh okislitel'nykh protsessov)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol. 121, Nr 1, pp. 141 - 144 (USSR)

ABSTRACT: The progressive development process of a malignant ulcer is very similar to the course of a unsteady chemical process, e.g. of the branched chain reactions (discovered by N.N.Semenov, Ref 1). It is possible that the observed similarities are based upon the similarity of the nature of the active intermediate substances responsible for the self-accelerating type of processes in vivo and in vitro. The active centers of the chain reactions yield the free radicals. In the slowly progressing (not explosive) branched chain reactions furthermore intermediate substances are formed which decompose sometimes under formation of free radicals. Consequently degenerated (retarded) ramifications are formed and the process is only to a small

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Leucosis in Mice and Some Characteristic Features of SOV/20-121-1-40/55
Its Development Under the Action of Certain Inhibitors of Oxidizing Chain
Processes

extent accelerated with respect to time. Certain data exist on the fact that the free radicals and the chain reactions play a rôle (Ref 2) in the mechanisms of several biochemical processes. It is especially important that the reactions of a biological (fermentative) oxidation which produce the energy necessary for the growth of the malignant ulcer are considered from this point of view. We may also assume that the free radicals in the biosubstrate stimulate the radical (chain-) reactions and thus represent in many cases the mechanism of cancer formation. A number of proofs of this assumption is given. All this leads to the conclusion that it might be expedient to act upon the malignant ulcers by the introduction of substances which react easily with free radicals (chain breakers). Strong, non-toxic inhibitors of the oxidizing chain reactions (nutrition antioxidants): I) Butyloxy-anisol (isomeric mixture); II) Ionol (2,6-di-tert. butyl-4-methyl phenol); III) Propyl gallate and others were tested by the authors as such substances. Leucoses with acute course which can be re-inocculated (perevivayemye) were used as disease

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Leucosis in Mice and Some Characteristic Features of Its Development Under the Action of Certain Inhibitors of Oxidizing Chain Processes SOV/20-121-1-40/55

in mice suffering from severe leucosis of the line afb, race Л IV, and in the mice of the line C_{57}, race ЛA which were practically immune from leucosis. The latter was achieved by the re-inocculation of leucosis which was caused in the C_{57} mice by x-ray irradiation. The healthy control animals did not show dyspepsy or other pathological changes after a single administration of the preparation. In the afb mice which were 8 weeks old a prolongation of life and a healing of the leucosis process was observed. After 14 days the blood was completely normalized. The cured mice were immune from further leucosis inocculations. If the above mentioned facts turn out to be right we may expect that the class of chemotherapeutics will be effective in a vast range of malignant ulcers. Ye.Ye.Pogosyants (Institute of Experimental Pathology and Cancer Therapeutics, Academy of Medical Sciences USSR - Institut eksperimental'noy patologii i terapii raka AMN SSSR) placed specimens suffering from leucosis at the author's disposal. There are 3 figures and 5 references, 4

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Leucosis in Mice and Some Characteristic Features of Its Development Under the Action of Certain Inhibitors of Oxidizing Chain Processes SOV/20-121-1-40/55

of which are Soviet.

ASSOCIATION: Institut khimicheskoy fiziki Akademii nauk SSSR (Institute of Chemical Physics, AS USSR) Laboratoriya anizotropnykh struktur Akademii nauk SSSR (Laboratory of Anisotropic Structures AS USSR)

PRESENTED: May 6, 1958, by N.N.Semenov, Member, Academy of Sciences, USSR

SUBMITTED: May 5, 1958

1. Leukemia--Therapy 2. Cancer research--USSR 3. Chemotherapeutic agents--Development 4. Chemotherapeutic agents--Materials 5. Chemotherapeutic agents--Test results

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5(4)

AUTHORS: Knorre, D. G., Mayzus, Z. K., SOV/20-123-1-33/56
Emanuel', N. M., Corresponding Member, Academy of Sciences, USSR

TITLE: On the Rate of the Degenerate Branching of a Chain in the Oxidation of n-Decane (O skorosti vyrozhdennogo razvetvleniya tsepi pri okislenii n-dekana)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 123, Nr 1, pp 123-126 (USSR)

ABSTRACT: The authors determined the above-mentioned rate by the method of inhibitors. The n-decane was oxidized in the liquid phase in an oxidation cell which was located in an oxygen flow. From the rate of oxidation conclusions were drawn as to the accumulation of hydrogen peroxides, the concentration of which was determined iodometrically. α-naphthol was used as inhibitor. A diagram shows the kinetic curves of the accumulation of hydrogen peroxides in the oxidation of n-decane at 130° in the presence of α-naphthol (2.10^{-6}M/ml), the α-naphthol being introduced at various instants of time. The forming of free radicals is sharply accelerated in the initial period of the reaction. The later the inhibitor is introduced, the shorter will be the induction period of oxidation.

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On the Rate of the Degenerate Branching of a Chain in the Oxidation of n-Decane SOV/20-123-1-33/56

After the introduction of α-naphthol into the n-decane about to oxidize, the solution gradually becomes yellow. If α-naphthol is introduced in comparatively advanced stages, precipitation is even brown. The compound produced has a characteristic spectrum in the visible domain with a maximum absorption at 420 mμ. The optical density of the solution attains a maximum, after which it decreases. The solution is therefore colored by means of an intermediate compound, which is formed by the participation of α-naphthol. An addition of the precipitation of this compound to the fresh n-decane showed that the intermediate compound acts as an inhibitor. The α-naphthol yield follows the reaction of zero-th order only up to a ~70% transformation, after which distinct deviations from the equation of the first order are observed. Several possible causes of this phenomenon are pointed out. The values of the rate of consumption of the inhibitor in the n-decane in the state of oxidation at 130° at a concentration 0.02 M/l of the hydrogen peroxide and at various concentrations of the inhibitor are given. This rate of consumption $d[I]/dt$ does not depend on the concentration of the inhibitor. The inhibitor does therefore

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not take part in the production of free radicals and is merely an "instrument" of measuring the quantity $w_p = -d[I]/dt$. A further diagram shows the dependence of the branching rate obtained in this way at 130° upon hydrogen peroxide concentration. Thus, direct proof was given of the fact that hydrogen peroxide is the most important factor causing branching in n-decane oxidation. For the temperature dependence of the rate constant it holds that

$$k = 6.10^8 \exp(-24800/RT)\text{sec}^{-1} .$$

Degenerate branching is probably a bimolecular reaction with a hydrocarbon $ROOH + HR \rightarrow RO\bullet + H_2O + R\bullet$. There are 3 figures and 6 references, 1 of which is Soviet.

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

SUBMITTED: July 10, 1958

Card 3/3

ZEYNALOV, B.K.; EMANUEL', N.M., prof., laureat Leninskoy premii, red.;
DOLGOV, V.I., red.izd-va

[Kinetics and mechanism of oxidation of the paraffinic distillate and practical uses of the oxidation products] Kinetika i khimizm okisleniia parafinistogo distilliata i ispol'zovanie produktov okisleniia v praktike. Baku, Izd-vo Akad.nauk Azerbaidzhanskoi SSR, 1959. 253 p. (MIRA 13:4)

1. Chlen-korrespondent Akademii nauk SSSR (for Emanuel').
(Paraffins) (Oxidation)

EMANUEL' N M

PHASE I BOOK EXPLOITATION SOV/3663

Akademiya nauk SSSR. Institut khimicheskoy fiziki

Okisleniye uglevodorodov v zhidkoy faze; sbornik statey (Oxidation of Hydrocarbons in the Liquid Phase; Collection of Articles) Moscow, Izd-vo AN SSSR, 1959. 334 p. Errata slip inserted. 2,200 copies printed.

Ed.: N. M. Emanuel', Corresponding Member, Academy of Sciences USSR; Ed. of Publishing House: K. M. Dyumayev; Tech. Ed.: I. F. Kuz'min.

PURPOSE: This collection of articles is intended for chemists interested in hydrocarbon oxidation reactions, particularly for those specializing in petroleum fuels.

COVERAGE: This collection of 35 articles represents the results of investigations over a period of several years on problems of hydrocarbon oxidation. The authors present their own theoretical and experimental data and also draw from current literature. No personalities are mentioned. References accompany most of the articles.

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Oxidation of Hydrocarbons in the (Cont.) SOV/3663

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Emanuel', N.M. [Institut khimicheskoy fiziki (Institute of Chemical Physics)]. Problem of Controlling Hydrocarbon Oxidation Chain Reactions in the Liquid Phase 9

This article gives the general characteristics of hydrocarbon oxidation processes and describes the various principles involved in accelerating branched chain reactions. The phenomena which accompany the oxidation reaction, including the macroscopic stages, are investigated from the point of view of their utilization for controlling chemical processes.

Meyzus, Z.K. [Institute of Chemical Physics]. The Role of Peroxides in Hydrocarbon Oxidation Processes in the Liquid Phase 35

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from ketone α-hydroperoxides.

Shlyapintokh, V.Ya., and N.M. Emanuel' [Institute of Chemical Physics]. Mechanism of the Optical Sensitization of Liquid-Phase Oxidation by Molecular Oxydation of 2, 7-Dimethyloctane 113

The combined effects of photochemical activation and the catalytic action of polyvalent metal (Cu^{2+} and Fe^{3+}) stereates on the oxidation of 2,7-dimethyloctane are investigated. Additions of metal salts play the role of photoinitiators. The authors detect reaction acceleration caused by the photolysis of Cu^{2+} and Fe^{3+} stereates, and confirm the formation of free radicals which cause this acceleration.

Tinyakova, Ye.I., F.A. Dolgoplosk, and V.N. Reykh [Institut vysokomolekulyarnykh soyedineniy AN SSSR (Institute of High Molecular Compounds, Academy of Sciences USSR; Vsesoyuznyy nauchno-issledovatel'skiy institut sinteticheskogo kauchuka (All-Union Scientific Research Institute of Synthetic Rubber)]. Oxidation-Reduction Systems for Initiating Oxidation Processes in Hydrocarbon Media and the Mechanism of Their Action 117

The authors show that oxidation-reduction systems, widely used for initiating low-temperature polymerization processes, can be successfully employed for initiating oxidation reactions. The role of polyvalent metal salts in the decomposition of peroxides and the oxidation of hydrocarbons is discussed.

Blyumberg, E.A., Z.K. Mayzus, and N.M. Emanuel' [Institute of Chemical Physics]. Liquid-Phase Oxidation of n-Butane at Near-Critical Temperatures and Pressures 125

The authors discuss the kinetics and chemistry of a purportedly new method for liquid-phase oxidation of n-butane. Initiating the reaction with NO_2 and catalyzing with $CoSt_2$ resulted in a shorter induction period by increasing the initial rate of chain growth. Acetic acid and methyl ethylketone are the principal products of the reaction.

Denisov, Ye.T. [Moscow State University imeni M.V. Lomonosov] Kinetics of Cyclohexane Oxidation Catalyzed by Cobalt Stearate 136

The author finds that the catalytic action of cobalt salts (stearates) both breaks down and initiates chain growth during the oxidation of cyclohexane. The relationship between these functions is substantially changed as the reaction develops.

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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-decanes is described. The authors determine the critical concentration of cupric stearate (~ 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 152

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)

SOV/62-59-1-4/38

AUTHORS: Blyumberg, E. A., Voronkov, V. G., Emanuel', N. M.

TITLE: Gaseous Initiation by Ozone During the Process of Paraffin Oxidation (Gazovoye initsiirovaniye ozonom v protsesse okisleniya parafina)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 25 - 29 (USSR)

ABSTRACT: In the present paper the authors investigated the problem of the applicability of ozone as a gaseous initiator in the oxidation of liquid phases. The method of oxidation described in (Ref 3) has been already applied. The paraffin "Kepsen" was oxidized from brown coal supplied by the German Democratic Republic. Experimental data show a number of particular features which occur in the addition of ozone during the oxidation of liquid hydrocarbons. The kinetic curves of the increase in the acid numbers in paraffin oxidation are presented in (Fig 1). The effect of the stimulation with which the reaction was excited at the beginning may be seen from it. If ozone acts in it for a longer period a very peculiar phenomenon is observed. The reaction is

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Gaseous Initiation by Ozone During the Process of Paraffin SOV/62-59-1-4/38
Oxidation

accelerated (the period of induction is shortened) while the limiting yield of acids is simultaneously reduced. Similar phenomena were also observed in the application of other stimulants. In this connection the experiments with uninterrupted transition of ozonized air were somewhat startling, for the respective kinetic curve indicates a reaction course with maximum velocity and a very high degree of oxidation. It was assumed that the process of oxidation changes in this case and oxidation is produced no longer by molecular oxygen but by ozone. If molecular oxygen participates in the reaction it is included only in very small quantities. (Fig 2) confirms the conclusion that a strong stimulation of the process causes, apart from its acceleration, a reduction of the transformation degree. Interesting results were obtained (Fig 3) by the application of different temperature conditions during the initial stage and the development of the oxidation process effected by a "shock" at the beginning. It may be seen from it that the kinetic curve of acid numbers does not vary in any case. At present, the paraffin is oxidized by means of the manganese oxide

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Gaseous Initiation by Ozone During the Process of Paraffin Oxidation SOV/62-59-1-4/38

catalyst under commercial conditions, whereby the process is very complicated, however. Production is simplified and continuous conditions of oxidation are established by the application of ozone as a gaseous initiator. It must be emphasized that oxidation by ozonized air ensures good quality of the oxidation product which meets the requirements called for synthetic fatty acids. Simultaneously a complete utilization of raw material will be achieved. For comparison some properties of the oxidation products synthesized in the presence of the manganese catalyst on the one hand and by uninterrupted oxidation with ozonized air on the other hand are shown in the table. These data were obtained at the laboratory of the Vsesoyuznyy nauchno-issledovatel'skiy institut zhirov (All-Union Scientific Research Institute of Fats) in the Shebekinskiy Kombinat under the supervision of N. K. Man'kovskaya. There are 3 figures, 1 table, and 15 references, 8 of which are Soviet.

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Gaseous Initiation by Ozone During the Process of Paraffin SOV/62-59-1-4/38
Oxidation

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: May 29, 1957

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SOV/80-59-1-28/44

AUTHORS: Berezin, I.V., Vagnor, G. and Emanuel', N.M.

TITLE: Paraffin Oxidation Initiated by Chlorine During the Initial Stage of the Reaction (Okisleniye parafina, initsiirovannoye khlorom v nachal'nyy period razvitiya reaktsii)

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Nr 1, pp 173-180 (USSR)

ABSTRACT: The method of stimulating liquid-phase oxidation reactions by means of small admixtures to the air of certain catalyzing gases (NO_2, HBr, etc) was named the method of gas initiation [Ref. 1]. The present investigation was aimed at establishing main regularities of the initiation effect caused by admixtures of chlorine in the oxidation process of lignite paraffin of the "Köpsen" type (East Germany). As the main products of oxidation are aliphatic acids, the principal attention was paid to the kinetics of their formation and accumulation. The results of experiments are presented in graphical form. It can be concluded that the gas initiation of the reaction by chlorine has a strong stimulating effect on the paraffin oxidation process; at that the initiation is brought about during a short initial period in the development of the process. The accumulation of acids is described by the kinetic curves obtained experimentally. It was established that the low maximum effect in the kinetic

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Paraffin Oxidation Initiated by Chlorine During the Initial Stage of the Reaction

curves of acid formation is due to the presence in "Küpsen"-type paraffin of aromatic substances.
There are 8 graphs, 1 diagram and 4 Soviet references.

SUBMITTED: December 20, 1956

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5(1,3), 21(8) SOV/153-2-4-12/32

AUTHORS: Burlakova, Ye. B., Dzantiyev, B. G., Sergeyev, G. B., Emanuel', N. M.

TITLE: Radiolytical Oxidation of Fat

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 4, pp 533 - 540 (USSR)

ABSTRACT: The investigation of the kinetics and processes of fat oxidation is necessary for an economical production technology of edible and technical fats and oils as well as for the investigation of the assimilation mechanism of the fats consumed by living organisms. The oxidation reaction of fats forms a chain reaction with degenerate ramifications (Semenov, N. N., Academician, Ref 1). It has been pointed out recently (Tarusov, B. N., Refs 2,3) that the oxidation processes proceeding in the lipoprotein phase of the cell structures play an important role in radiation damage of the organism. The initiation of oxidative chain reactions can be achieved by a short effect of catalysts (initiators) at the beginning of the reaction (Refs 4,5). This phenomenon has many analogies in the developmental dynamics of radiation damages (Ref 6). Purified fresh cod-liver oil was

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chosen for the investigation. It was oxidized by means of atmospheric oxygen at 20-130° in a glass cell (Ref 7). It was irradiated with gamma rays from Co^{60} X-rays, and beta particles from P^{32} and Au^{198}. Figure 1 shows typical kinetic curves of the peroxide aggregation with thermal oxidation at 65-100°. They are characterized by an induction period which is shortened with increasing temperature: 8 hours at 65°; the period is almost entirely missing at about 100°. The curves of acid aggregation seen in figure 2 are analogous to the above curves. Acid formation, however, is somewhat retarded since acids are secondary oxidation products (Ref 9). The effect of ionizing radiations on fat containing dissolved oxygen leads to the appearance of oxidation products already at room temperature. The intensities of oxidation in the range of doses used, however, are not high ($D = 10^3 - 10^5$ p). The extent of the effect depends on the temperature at which the fat is irradiated. The yield rises with increasing temperature (Figs 3,4). This seems to be connected with the attaining of conditions favoring the chain extension (Fig 3). The authors introduce the symbol G for the value of the radiation effect. Equations are derived for G as well as for the reaction rate W. Curve 1 (Fig 5) concerning the oxidation

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of irradiated and nonirradiated fat at 100° illustrates the presence of an "upper temperature limit". Above this limit the irradiation dose does no longer affect the oxidation kinetics. The effect of a previous irradiation at 20° on the formation kinetics of peroxides in fat with an oxidation at a higher temperature is analogous (Fig 6). Thus, the separation of the irradiation period and the oxidation period with respect to time only affects the duration of the induction period whereas the chemism of the process remains unchanged. The types of radiation mentioned at the beginning neither influence the kinetics nor the chemism of fat oxidation. The quantity of radiation yield depends on the temperature extreme. There are 8 figures and 11 references, 8 of which are Soviet.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet imeni M. V. Lomonosova, Kafedra khimicheskoy kinetiki (Moscow State University imeni M. V. Lomonosov, Chair of Chemical Kinetics)

SUBMITTED: May 16, 1958

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5(4)

AUTHORS: Kruglyakova, K. Ye., Emanuel', N. M. SOV/62-59-3-6/37

TITLE: Some Particular Features in the Behavior of Intermediate Molecular Substances During Propane Oxidation (Osobennosti povedeniya molekulyarnykh promezhutochnykh veshchestv pri okislenii propana)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 417-424 (USSR)

ABSTRACT: In the present paper the attempt was made to explain the role of some oxidation products - acetaldehyde, methyl alcohol, acetic acid - during the development of the reaction by kinetic methods. Besides, the problem of the nature of the maximum yield of one of these products (acetaldehyde) was experimentally investigated. In figure 1 the kinetic curves of the formation of intermediate products are presented. Under given experimental conditions it could be seen that propane is consumed during the formation of acetaldehyde, formaldehyde, and methyl alcohol in practically equal quantities. The effect exerted by acetaldehyde additions (1.78, 4.3, 5.5 %) on the formation kinetics of the intermediate products is given in figure 2. It was proved that these additions increase the

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oxidation rate of propane, whereby acetaldehyde, formaldehyde, and apparently methyl alcohol are formed. The maximum concentrations of the oxidation products remain the same as in experiments without additions. The addition of acetic acid (0.28 %) and methyl alcohol (2.7 %) does not affect their yield (Table). By means of tagged atoms it was proved that the maximum concentration of acetaldehyde represents a special case of the dynamic equilibrium. Apparently in the moment of the maximum concentration both the formation and consumption of this product are retarded. This might be due to an interaction of the intermediate products with the radicals of the chain, wherein less active centers are formed which guarantee the retarding effect. The lacking activity in dimedone derivatives of formaldehyde confirms the assumption that the latter is not formed from acetaldehyde but independently of it. The value of the specific activity of carbon monoxide $\alpha = 125$ impulses per minute . mg and CO_2 (132 impulses per minute . mg) indicates that CO and CO_2 are not only formed from

Some Particular Features in the Behavior of Intermediate Molecular Substances During Propane Oxidation SOV/62-59-5-6/37

acetaldehyde but also in another way. There are 4 figures, 1 table, and 18 Soviet references.

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

SUBMITTED: May 30, 1957

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SOV/62-59-6-8/36

5(4)

AUTHORS: Kruglyakova, K. Ye., Emanuel', N. M.

TITLE: Kinetics of the Oxidation of Propane Induced by Chlorine in Packed Vessels at Different S/V (Kinetika initsiirovannogo khlorom okisleniya propana v sosudakh s nasadkoy pri raznykh S/V)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1005 - 1010 (USSR)

ABSTRACT: By way of introduction the different possibilities of observing the chain reaction which occurs with the process mentioned in the title are dealt with in brief (Refs 1-17). It could be observed that a considerable influence is exercised upon the process by the walls of the vessel, that is to say, by their shape and the material they are made of. For the investigation reported on in the present paper a vessel was used made of sodium glass which was equipped with an insert consisting of glass balls of the same type but with different diameters (5,3,1.7 mm). Oxidation was investigated with a mixture of $C_3H_8:O_2=1:1$ at a temperature of 346°, at first in a vessel without an insert. (Curves of the reaction kinetics in figure 1).

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In this case already no agreement with the data given in reference 18 could be found. (These data were obtained by using a quartz vessel for the reaction). When using the ball shaped inserts the reaction was considerably accelerated (mostly if the balls had a diameter of 1.7 mm), but on the other hand the yield in aldehydes decreased. It is because of this acceleration that the reaction may also be carried out in the presence of chlorine without inflammation of the mixture (Fig 2). In this case the chlorine (0.5%) despite of its accelerating the process also secures a high yield in aldehydes. The kinetic curves which all (with, and without addition of chlorine that only influences the yield in aldehydes) exhibit an S-shape may easily be represented by the autocatalytic function of the first order, if only not the initial but the final concentration of the product is taken as standard for the reaction intensity. Thus the reaction is self-accelerating and the insert only influences the ramification of the chains as with this ball shaped insert a reaction surface is formed which takes part in the process of ramification. The peroxide which otherwise

Kinetics of the Oxidation of Propane Induced by Chlorine in Packed Vessels at Different S/V SOV/62-59-6-8/36

as intermediate product disturbs the reaction may without any difficulties be decomposed on the burning surface. There are 8 figures and 18 references, 13 of which are Soviet.

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

SUBMITTED: August 23, 1957

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5 (2), 5 (4)

AUTHORS: Kruglyakova, K. Ye., Emanuel', N. M. SOV/62-59-7-9/38

TITLE: Activation of the Container Surface by the Reacting Mixture $C_3H_8 + O_2$ in the Presence of Chlorine (Aktivatsiya poverkhnosti sosuda reagiruyushchey smeys'yu $C_3H_8 + O_2$ v prisutstvii khlora)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1211-1215 (USSR)

ABSTRACT: By way of an introduction there is a brief reference to own papers and to papers of Sergeyev and Shtern (Ref 2), Kalinenko and Voyevodskiy (Ref 3) being in connection with the problem under review. This paper reports on the discovered activation effect as it is called in the title. The existence of the effect was concluded from the initiating effect of the surface of the container on the oxidation in the absence of chlorine following experiments with chloroinitiated oxidation of propane.

The apparatus on which the experiments were carried out is described in paper, reference 5. The reaction kinetic curves with and without the addition of chlorine at 335° are plotted in figure 1. The chlorine influences strongly the yield of acetaldehyde. This influence of the chlorine could only be

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Activation of the Container Surface by the Reacting Mixture $C_3H_8 + O_2$ in the Presence of Chlorine SOV/62-59-7-9/38

noticed in quartz containers with a glass splinter filling. In containers made of other material also the formation of formaldehyde was influenced. There are accordingly two ways independent of one another to produce both aldehydes. A production scheme of both aldehydes is given (for the formaldehyde according to the scheme of Semenov and Shtern (Refs 4, 6)). Furthermore, the yield of formaldehyde and acetaldehyde is investigated in dependence on the reaction temperature and addition of chlorine. In figure 3 also the secondary effect of chlorine is to be seen (decrease of the yield of aldehydes at high temperatures). There are 4 figures and 6 Soviet references.

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

SUBMITTED: October 24, 1957

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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 SOV/62-59-8-6/42

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: $i\text{-}C_4H_{10}+O_2 \rightarrow (CH_3)_3COOH$, $(CH_3)_3COOH + (CH_3)_3CH \rightarrow (CH_3)_3COH + (CH_3)_2CO + CH_4$. 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: December 27, 1957

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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 Azerbaydzhanskoy SSR M.F. Nagiyevym.
(Propane) (Oxidation)

BEREZIN, I.V.; VAGNER, G.; EMANUEL', N.M.

Chlorine-initiated oxidation of paraffin. Zhur.prikl.khim.
32 no.1:173-180 Ja '59. (MIRA 12:4)
(Paraffins) (Oxidation) (Chlorine)

5(3)

SOV/80-32-4-33/47

AUTHORS: Berezin, I.V., Denisov, Ye.T., Suvorova, S.N., Smolyan, Z.S. and Emanuel', N.M.

TITLE: The Oxidation of a Mixture of Cyclohexane and Cyclohexanol to Adipic Acid (Okisleniye smesi tsiklogeksana i tsiklogeksanola v adipinovuyu kislotu)

PERIODICAL: Zhurnal prikladnoy khimii, 1959, Vol 32, Nr 4, pp 888-892 (USSR)

ABSTRACT: Production of monomers for plastics and synthetic fibers is one of the important tasks of modern chemistry. The utilization of various waste materials can contribute to the solution of this task. One of these waste materials is the mixture of cyclohexane, 80 mol.%, and cyclohexanol, 20 mol.%. The authors studied the kinetics of the oxidation of this mixture, called "anol head", with an aim of obtaining cyclohexane and adipic acid. The oxidation was carried out in an autoclave at a pressure of 20 atm by molecular oxygen at temperatures of 130 and 150°C. Kinetic curves of accumulation of the reaction products were obtained and the possibility of producing adipic acid by oxidizing the "anol head" was proven. It was shown that some peculiarities in the oxidation kinetics were determined wholly by the concentration of cyclohexanol

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The Oxidation of a Mixture of Cyclohexane and Cyclohexanol Into Adipic Acid

in the "anol head". The process of oxidizing "anol head" is to be carried out with continuous removal of adipic acid obtained in order to prevent its burning into lower dicarboxylic acids, and the process thereby acquires a continuous character. There are 3 sets of graphs and 7 Soviet references.

SUBMITTED: November 1, 1957

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