5(4) SOV/76-33-1-36/45

AUTHORS: Knorre, D. G., Mayzus, Z. K., Markin, M. I., Emanuel', N. M.

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 mμ 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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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/76-33-2-25/45

AUTHORS: Knorre, D. G., Mayzus, Z. K., Markin, A. I., Emanuel', N. M.

TITLE: Kinetics of the Reaction Between Decyl Hydroperoxide and Manganous Stearate in n-Decane (Kinetika vzaimodeystviya gidroperekisi detsila so stearatom margantsa v n-dekane)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 2, pp 398 - 404 (USSR)

ABSTRACT: Several papers on the oxidation kinetics of hydrocarbons involving manganese or cobalt catalysts report that the catalyst is observed to assume a higher valence number. In regard to this several hypotheses have been set forth by Ye. T. Denisov and N. M. Emanuel' (Ref 6), B. V. Yerofeyev and L. I. Chirko (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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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 85°C show that a maximum transformation occurs with ratios of (I): decyl hydroperoxide (II) of 9.7-80%, at 4.83-56%, and 3.23-40%. 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 rule of the induced decomposition of (II) is unknown only the upper limit of the activation energy could be reliably determined (22.5 kcal), but for a first approximation of the activation energy a value of 18 kcal was obtained. The rate constant for the reaction giving an accumulation of the colored reaction product (oxidized form of (I)) is written as

Card 2/3 $k = 2.8.10^{11} e^{-18000/RT}$ 1/mole.sec. There are 7 figures and

Kinetics of the Reaction Between Decyl Hydroperoxide and Manganous Stearate in n-Decane SOV/76-33-2-25/45

12 references, 5 of which are Soviet.

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)

AUTHORS: Knorre, D.G., Chuchukina, L. G., Emanuel', N.M. SOV/76-33-4-20/32

TITLE: On the Phenomenon of Critical Concentration of $Cu(C_{17}H_{35}COO)_2$ in the Reaction of Catalytic Oxidation of n-Decane (O yavlenii kriticheskoy kontsentratsii $Cu(C_{17}H_{35}COO)_2$ v reaktsii katalizirovannogo okisleniya n-dekana)

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 4, pp 877 - 882 (USSR)

ABSTRACT: In the present paper a new example is given of the critical phenomena in reactions with degenerated branchings in liquid phase which were observed in the investigations of n-decane oxidation in the presence of copper stearate (I). At a certain concentration of (I) a complete stop of the reaction was observed while at this concentration a self-accelerated reaction with a small induction period takes place. n-decane (II) was produced electrolytically (Ref 5) and (I) according to a method of production described. (I) and (II) were dissolved in a nitrogen current and the moment where oxygen was introduced was regarded as the beginning of reaction.

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of $Cu(C_{17}H_{35}COO)_2$ in the Reaction of Catalytic Oxidation of n-Decane

0.03 - 0.10 mol% of (I) were used and the peroxides, carbonyl compounds, acids, and copper were determined according to the course of oxidation; the latter according to two methods: Cu^{2+} and the entire copper. A catalytic effect (Fig 1 for 0.03% (I)) could be observed until a concentration of 0.06 mol% (I) is attained. A change in the copper valency in the induction period is explained by a reaction of (I) with intermediate oxidation products of (II) (e.g.hydrogen peroxides) which causes the self-acceleration proper of the process. The increase of the induction period at an increase of concentration of (I) is indicative of a second- the inhibiting - effect of (I) which apparently is based on a destruction of the chains at the (I)-molecules. The critical concentration is at 0.065 mol% (I) at which the induction period is longer than 15 hours and where the oxidation rate also changes. The phenomenon of the critical concentration of (I) is explained by the radical-chain-mechanism of hydrocarbon oxidation. There are 5 figures, 1 table, and 9 references, 6 of which are Soviet.

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On the Phenomenon of a Critical Concentration SOV/76-33-4-20/32
of Cu($C_{17}H_{35}COO)_2$ in the Reaction of Catalytic Oxidation of n-Decane

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

SUBMITTED: September 28, 1957

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5(4) SOV/76-33-7-29/40

AUTHORS: Gagarina, A. B., Emanuel', N. M.

TITLE: Kinetic Rules Governing the Reaction of Methane and Nitrogen Dioxide

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 7, pp 1641 - 1647 (USSR)

ABSTRACT: Small additions of NO_2 to air or oxygen in gaseous-liquid phase oxidations of hydrocarbons are known to have a strong stimulating effect (Refs 1,2). Among numerous articles on the reaction of paraffins and NO_2 there are only two (Refs 9, 10) dealing with the kinetic treatment of this process. Since an unsuitable method was applied in (Ref 10), the authors investigate in this article the afore-mentioned subject within the temperature range where NO_2 dissociates noticeably. For this purpose, an ordinary static vacuum apparatus was used, i.e. a reaction cylinder (15 cm long, volume of 200 cm^3). The authors applied a method by which the reaction vessel was filled with CH_4 as soon as the dissociation of the previously introduced

Card 1/2 NO_2 was in equilibrium. The kinetic rules governing the reaction

Kinetic Rules Governing the Reaction of Methane and Nitrogen Dioxide SOV/76-33-7-29/40

were determined by plotting kinetic curves on the basis of the pressure rise (measured by means of a diaphragm gauge) as well as of NO_2 consumption (photocolorimetrically determined). Measurements were made at 360 - 420° and an initial CH_4 pressure of 50, 100, 200 and 300 torr. The authors further made experiments with additions of NO or oxygen. Experimental results led to the following conclusions: The rate of the total pressure rise of the zero-th order, whereas that of the initial pressure of CH_4 is of the first order. The pressure rise is accelerated by NO additions, while the addition of oxygen strongly inhibits the reaction. The resultant effective activation energy of the process amounts to 42 kcal/mol. There are 9 figures and 10 references, 5 of which are Soviet.

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

SUBMITTED: February 21, 1958

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SOV/76-33-8-33/39

5(4)

AUTHORS: Gagarina, A. B., Emanuel', N. M.

TITLE: Kinetics and Chemism of the Reaction of Methane With Nitrogen Dioxide

PERIODICAL: Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 8, pp 1872-1879 (USSR)

ABSTRACT: In continuation of a previous paper, an investigation of the intermediate and final products of the reaction between methane (I) and nitrogen dioxide (II) was carried out and the kinetic behavior of the reaction products was examined. Besides the analytical methods described in publications, analysis methods particularly developed for that purpose were used as well. The analyses showed that the reaction products are nitromethane (III), CO (IV), CO_2 (V), NO (VI), and traces of formaldehyde, and HCN (VII). The kinetic behavior of these substances was examined in a static vacuum unit with a reaction vessel made of molybdenum glass (200 cm^3). The kinetics of the formation of (III) was examined thoroughly. It was found that (III) forms as an intermediate product and further decomposes. A complete analysis of the reaction

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Kinetics and Chemism of the Reaction of Methane With Nitrogen Dioxide

products rendered it possible to determine a material balance with respect to carbon and nitrogen (Table 1). The following rate constant is suggested:

$$w = k\frac{[CH_4][NO_2]}{[O_2]}$$

(k = summary rate constant, $[CH_4]$, $[NO_2]$ and $[O_2]$ = pressures of (I), (II), and oxygen). Data for the value of w/k are given in mm Hg for up to 15 minutes after the beginning of the reaction (Table 2). Various thermodynamic constants relating to the reaction investigated are computed, and it is found that the reaction of (I) and (II) follows two separate directions - the nitration of (I) while (III) forms, and the intensive oxidation of (I) with the oxygen from (II), while (IV) and (V) are formed. There are 4 figures, 2 tables, and 12 references, 4 of which are Soviet.

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

SUBMITTED: February 21, 1958

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SOV/26-59-1-19/34

AUTHOR: Emanuel', N.M., Corresponding Member, AS USSR

TITLE: The Control of Chain Reactions in Chemistry (Upravleniye tsepnymi reaktsiyami v khimii)

PERIODICAL: Priroda, 1959, 48 Nr 1, pp 46 - 56 (USSR)

ABSTRACT: The article gives a historical and physical survey on the phenomenon of chain reactions in chemistry and stresses especially the merits of Academician N.N. Semenov and his investigations of catalyzers and inhibitors in chemical chain reactions, which he carried out in the thirties and for which he was awarded the Nobel Prize in 1956. These fields of the mechanism of chemical reactions and chemical kinetics have assumed new importance with respect to the objectives of the 7-Year Plan in the field of synthetic-material production. The author, together with Z.K. Mayzus, K.Ye. Kruglyakova, M.F. Sedova and other researchers, discovered interesting pecularities of the action of positive catalyz-

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The Control of Chain Reactions in Chemistry SOV/26-59-1-19/34

ers in oxidation chain reactions of hydrocarbons. In addition to formerly known elementary reactions, aggregate interactions take place. The reaction mechanisms on their way from one macroscopic stage to the next and the occurring changes were studied (Figure 1). Ye.T. Denisov together with the author succeeded in increasing the yield of cyclohexanone by over two times by merely removing the catalyzer from the reaction zone after an initiator action of brief duration. While new concepts, with respect to sudden breaks of chain reactions on the walls of the reaction vessel, were found by **Professor** A.B. Nalbandyan in 1946 together with the possibility of influencing these breaks (Figure 2) similar to effects upon nuclear reactions, **Corresponding Member AS USSR** A.A. Koval'skiy discovered solid surfaces that bring about a chain reaction process. Concepts on these homogeneous-heterogeneous reactions had been formed earlier by Professor M.V. Polyakov. Recently, Academician N.N. Semenov, **Corresponding Member AS USSR** V.V. Voyevodskiy and **Professor** F.F.

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Vol'kenshteyn formed new concepts on reactions of a merely heterogeneous catalysis by way of the chain mechanism brought about by free radicals. If these concepts can be proved by experimentation, new ways of influencing the processes of the heterogeneous catalysis would be given. Speeding up of slow reaction processes by way of diverse stimulation (Figures 3-6) is being studied by Professor N.A. Proskurnin, E.A. Blyumberg, D.M. Ziv, V.L. Rikayeva, V.K. Tsyskovskiy, V.K. Zeynalov, and the author. The problem of free radicals and chain reactions in biological processes is being studied by L.P. Lipchina and Professor B.N. Tarusov (Figures 7 and and 8). The author concludes that there are various ways of influencing chemical and biochemical chain reaction processes, many of which may lead to inter-

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esting results and further possibilities. There are 8 graphs and 1 Soviet reference.

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

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17(3) SOV/20-124-5-56/62

AUTHORS: Emanuel', N. M., Corresponding Member, AS USSR, Lipchina, L. P., Pelevina, I. I., Lipatova, T. E.

TITLE: The Selective Inhibition of the Activity of Reduction-Oxidation Enzymes in Tumoral Cells When Acted Upon With Inhibitors of Chain Reactions (Izbiratel'noye podavleniye aktivnosti okislitel'no-vosstanovitel'nykh fermentov v opukholevykh kletkakh pri vozdeystvii ingibitorov tsepnykh reaktsiy)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 5, pp 1157-1159 (USSR)

ABSTRACT: Since many years the idea of a selective inhibition of fermentative processes in tumoral cells, as a rational principle in cancer chemotherapy, focuses the interest of the scientists (Ref 1). The first two authors (Ref 2) proved an inhibition and a retrogression of leucosis in mice under the action of non toxic inhibitors of the oxidative chain reactions (butyl-oxy-anisole, ionone, propyl gallate)(Ref 2). There were reasons (the radical mechanism of the reduction-oxidation processes) for assuming that the inhibition mentioned in the title is one of the reasons of the tumor inhibiting effect of the mentioned substances. This disturbs the formation processes of some energy-rich compounds which are necessary for the

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intense biosynthesis in the neoplastic growth. In the present paper results could be obtained which confirm the above assumption. The authors investigated enzymes of the succinoxidase system. The ascitic cancer of Ehrlich (Erlikh) in mice, leucosis of black mice (line C-57, strain LA), acridine sarcoma of mice and the Braun-Pirs tumor of rabbits served for the experiments. Cells of the ascitic cancer as well as tumoral tissues of other new formations reduced to small pieces were incubated for 30 minutes in 0.75, 0.15 and 0.075% propyl gallate solution. These concentrations inhibit the activity of succine dehydrogenase in the cells of all tumors investigated (Figs 1, 2). The activity of this enzyme is not suppressed in healthy liver and spleen cells by propyl gallate solutions of 0.15 and 0.075% (Figure 3). Incubation in a 0.75% solution is, however, inhibiting. This inhibition is reversible in afflicted as well as in sound cells. The differences in the propyl gallate effect on the reduction-oxidation processes in normal and tumoral cells are probably due to a different permeability of the cells and their components (e.g. mitochondria)

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to propyl gallate. Thus, propyl gallate has a selective effect on tumoral cells in certain concentrations. This is expressed by the inhibition of the activity of dehydrogenases which participate in various reduction-oxidation processes as well as of cytoochromoxidase. The thus influenced cells loose their implantation power. There are 3 figures and 6 references, 5 of which are Soviet.

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

SUBMITTED: November 25, 1958

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5(4) SOV/20-124-6-21/55

AUTHORS: Vasil'yev, R. F., Karpukhin, O. N., Shlyapintokh, V. Ya., Emanuel', N. M., Corresponding Member, AS USSR

TITLE: Gas Initiation by Ozone in the Reaction of the Oxidation of Isodecane and the Chemiluminescence Connected With It (Gazovoye initsiirovaniye ozonom v reaktsii okisleniya izodekana i svyazannaya s nim khemilyuminestsentsiya)

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

ABSTRACT: The present paper deals with the stage of initiation by ozone in segregated form, i.e. the authors investigate such phenomena and processes as occur during the short action of the initiator. Isodecane (2.7-dimethyl-octane) was used as test object. Preliminary tests showed that if ozone is blown past during a short time the reaction is accelerated considerably. The authors recorded a weak glow which was produced during the bubbling of oxygen (containing 2-3 % ozone) by isodecane. This isodecane was in a glass oxidation cell at temperatures of 20-90°. By glow the photomultiplier FEU-19 served as an indicator of the glow. The photoelectric current was recorded

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

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

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

SUBMITTED: October 29, 1958

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17(3) SOV/20-125-2-49/64

AUTHORS: Emanuel', N. M., Corresponding Member, AS USSR, Lipchina, L. P., Pelevina, I. I.

TITLE: Selective Decrease of the RNA Content in Tumor Cells and Their Loss of the Ability to be Grafted when Acted upon by Chain-reaction Inhibitors in Vitro (Izbiratel'noye umen'sheniya soderzhaniya RNK v opukholevykh kletkakh i poterya imi sposobnosti privivat'sya pri vozdeystvii in vitro ingibitorov tsepnykh reaktsiy)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 2, pp 411-413 (USSR)

ABSTRACT: The authors found a principal possibility of the inhibition and retrogression in the formation of tumors by use of the aforesaid inhibitors (Ref 1). The activity of important redox ferments in tumor cells is suppressed by propyl gallate in vitro (Ref 2). Thus these cells are deprived of the energy they need for intense biosynthetic processes which are typical of blastoma growth. Among these processes the biosynthesis of ribonucleic acid (RNA) is of special interest, which, according to modern views, forms a matrix for albumin synthesis (Ref 3). There is a certain connection between the

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Selective Decrease of the RNA Content in Tumor Cells SOV/20-125-2-49/64
and Their Loss of the Ability to be Grafted when Acted upon by Chain-reaction
Inhibitors in Vitro

intensities of albumin synthesis and the re-formation of RNA. Also rapidly growing cells of tumor are known to possess a high RNA content (Refs 4-6). There are also some indications (Ref 7) that the decrease of RNA content below a certain value stops albumin synthesis. In the present paper it was found that a considerable selective decrease of the RNA content in tumor cells is caused by propyl gallate (as compared to a regular cell) so that these cells lose the capability of being implanted. Ehrlich- (Erlikh-) cancer of mice, carefully minced tissues of leucosis mice, Brown-Pierce- (Braun-Pirs-) tumor of rabbits, acridine sarcoma of mice, sarcoma 45 of rats and Rous-sarcome of hens were used for the experiments. Already after an action of 0.75 % propyl gallate solutions for 15-30 min neither plasm RNA nor nuclear RNA is visible under the luminescence microscope (Fig 1 a,b). The change of the RNA content are reversible and can be eliminated to a certain extent (Fig 1, v). Experiments with sound liver cells have shown that the inhibitor (0.15 %) insignificantly reduces the RNA content within a short time;

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on the other hand, a complete adaptation of the cells follows and the regular state is restored (Fig 2 a,b). Thus it was possible to draw the important conclusion on the selective effect of propyl gallate on tumor cells, which explains the therapeutical effect of the inhibitor in vivo without damage of the organism as a whole. The cells of the enumerated tumors are therein completely deprived of the capability of implantation. If they are washed out with physiological common salt solution, this lost capability is restored. There are 2 figures and 8 Soviet references.

SUBMITTED: November 25, 1958

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17(3)

AUTHORS: Emanuel', N. M., Corresponding Member AS USSR, SOV/20-125-5-53/61
Lipchina, L. P.

TITLE: The Loss of the Blastomagenic Properties of the Virus of Rows' Sarcoma Under the Action of Propylgallate (Poterya blastomagennykh svoystv virusa sarkomy Rousa pri vozdeystvii propilgallata)

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 125, Nr 5, pp 1148-1150 (USSR)

ABSTRACT: Several malignant tumors are known which can be revaccinated not only by the transplantation of tumor cells, but also by the introduction of filtrates of tumor tissues free from cells. This capacity vanishes after the influence of one of the inhibitors of the oxidative chain processes, of propylgallate (Ref 1). This does, however, not occur in consequence of the protein denaturation. The cells from which the inhibitor was washed out with physiological sodium chloride solution become anew blastomagenic. This is as well the case with cells (Ref 2) of such tumors which can be revaccinated by means of filtrates free from cells (Rows' sarcoma of fowls, mouse leucosis). The authors are with respect to the rôle of the free radicals in the growth processes of the tumor (Ref 3) of the opinion that the spreading of the virus takes in many cases place by the transformation of the cell cytoplasm, not by separation

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The Loss of the Blastomagenic Properties of the Virus of Rows' SOV/20-125-5-53/61
Sarcoma Under the Action of Propylgallate

(Ref 4). In such cases the progressive virus propagation has a character similar to the nonsteady chemical processes which are stimulated by free radicals (Ref 5). The references 6,7 deal with the possible autocatalytic character of the virus spreading. A slight inactivation of the virus by the oxidation with oxygen is as well interesting (Ref 8). All that may prove free-radical character of the virus particles. Thus may be assumed that the loss mentioned in the title after the influence of the inhibitors is related to the loss of the free-radical properties by the virus. As a consequence of this may be assumed that an inactivation of the tumor forming viri and the loss of the blastomagenic properties of filtrates free from cells is possible by the influence of inhibitors of the free-radical (chain) processes. The addition of propylgallate did not cause abrupt shifts of the pH-value in the experiments of the authors (it remained between 6.7 and 6.9). The filtrates (control with 1:1 physiological sodium chloride solution and experiment with propylgallate in an equal solution: 0.75, 0.15, and 0.075%) were kept 30 minutes in the propylgallate solution on ice. Experimental- and control material was at the same moment injected into the right or left wing respectively of one and the

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same fowl. The latent period up to the formation of the tumor took 7-12 days in the case of the filtrate without propylgallate. The fowls died after 18-20 days. As a rule, no tumor was produced in the case of a filtrate inhibited with 0.75% propylgallate (Fig 1,a,b). Only 3 of 30 fowls had tumors the rate of growth of which was, however, to a great extent inhibited (pea-sized instead of chicken egg-sized like in the control). 0.15% propylgallate lead to an inhibited tumor formation, whereas 0.075% was inactive. Finally the authors make the attempt of interpreting the obtained results. Propylgallate suppressed the activity of the redox ferments, e. g. of the dehydrases. R. M. Radzikhovskaya helped in this investigation. There are 1 figure and 14 references.

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

SUBMITTED: February 11, 1959

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5(4) SOV/20-128-4-33/65

AUTHORS: Denisov, Ye. T., Mayzus, Z. K., 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 CO_2 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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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

S/595/60/000/000/004/014
E196/E535

AUTHORS: Emanuel', N.M., Berezin, I.V. and Denisov, Ye.T.

TITLE: The oxidation of cyclohexane

SOURCE: Vsesoyuznoye soveshchaniye po khimicheskoy pererabotke neftyanykh uglevodorodov v poluprodukty dlya sinteza volokon i plasticheskikh mass. Baku, 1957. Baku, Izd-vo AN Azerb.SSR, 1960, 143-156

TEXT: The kinetics of oxidation of cyclohexane were investigated without using catalysts, with catalytic salts and with a stimulating gaseous initiation. The aim of this study was to gain more information on the oxidation of cyclohexane which is important in the production of cyclohexanone and adipic acid for the nylon fibre industry. A further aim was to determine the laws governing this simple liquid phase oxidation and to apply these laws to more complicated hydrocarbons. Without a catalyst satisfactory velocities can be attained at pressures of 10-100 atm and temperatures of 135-155°C. The main intermediate products are cyclohexanone, cyclohexanol and cyclohexyl hydroperoxide. A second liquid phase appears when the reaction mixture becomes

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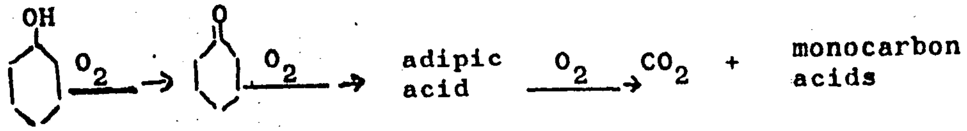
saturated with water and adipic acid, which have limited solubilities in cyclohexane. As the reaction is a chain degradation-branching reaction, no single parameter can be used to characterize it. The maximum absorption rate of oxygen is a function of temperature and obeys the Arrhenius equation, with an activation energy of 27 kcal/mol. The log of the conversion coefficient to cyclohexyl hydroperoxide over the first part of the reaction varied linearly with the inverse of the temperature, with activation energy 29 kcal/mol. For the intermediate cyclohexanone, the log maximum concentration varied linearly with the inverse of the temperature, the activation energy being 8 kcal/mol. The transformation of the intermediate products was studied by the use of radioactive carbon as marker and the following sequence was found



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In glass vessels the hydroperoxide breaks down equally into cyclohexanol, formed entirely by the decomposition of cyclohexyl hydroperoxide, and cyclohexanone, from decomposition of the hydroperoxide and oxidation of cyclohexanol. Adipic acid is formed exclusively by oxidation of cyclohexanone whilst the esters are formed by direct esterification of the adipic acid with cyclohexanol. In a steel vessel, however, cyclohexanone is also formed by decomposition of the cyclohexyl hydroperoxide radical. In the reaction with catalyzing salts, cobalt stearate dissolved in cyclohexane was used as catalyst. During the reaction, the cobalt changes into the trivalent state, and after a few minutes at 130°C the concentration of Co(III) becomes constant, then begins to decrease until after about 1.5 hours it is all once more in the divalent state. With the appearance of adipic acid the cobalt begins to precipitate as cobalt adipate, but part of the catalyst remains in solution throughout the reaction. The catalyzed and non-catalyzed oxidations differ as regards the reaction rate and concentrations of the intermediate products. Experiments with different concentrations of

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the catalyst (0.06 to 0.00023 mol %) showed that the higher the amount of catalyst, the faster the rate of reaction, demonstrating that, in the initial periods, it is a chain reaction whose rate of initiation is proportional to the concentration of dissolved catalyst. Similar results were obtained using cobalt adipate. The catalyst has thus two functions - initiation of the reaction and regulation of the proportions of the products. The rate of absorption of oxygen in the uncatalyzed reaction remains constant after the induction period; in the catalyzed reaction it rises to a maximum and then decreases to a constant value which is less than that of the uncatalyzed reaction. This suggests a self-delaying action. To confirm this supposition the catalyst was removed from the reaction zone some time after initiation and the final constant velocity attained was found to be higher than for the uncatalyzed reaction. A new method of stimulating liquid phase oxidation, using NO_2, was studied. The air was saturated with NO_2 (0.4%) at a rate of 50 litres/hr. At 140°C the reaction was markedly accelerated. The method was also tried in combination with cobalt stearate catalyst. A table is

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included which gives yields of acid and ketone for the various methods of oxidation. A mathematical analysis of the reaction is made on the assumption that it is a simple chain reaction with a single intermediate and a single final product; the chain is assumed to be broken by recombination of the free radicals. Academicians B. A. Kazanskiy, G. S. Landeberg and N.N.Semenov are mentioned in the paper. There are 10 figures and 2 tables.

Table

Test	Depth of oxidation	Yield of acid,%	Yield of ketone,%
Autooxidation	14.8	30	37
Oxidation with St_2Co	18.5	58	23
Oxidation with NO_2	19	57	22
Oxidation with $St_2Co + NO_2$	22	51.5	27

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82654

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

5.3200

AUTHORS: Mayzus, Z. K., Skibida, I. P., Emanuel', N. 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 - - $1.9 \cdot 10^{-3}$ min.$^{-1}$. It is near the value of the reaction rate constant of the reaction chain branching in the oxidation of n-decane (K =$1.1 \cdot 10^{-3}$ 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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Chain- and Molecular Reactions of Intermediates in the Oxidation of n-Decane

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

with the $RO_2^{\cdot}$ radical but also with $RO^{\cdot}$ 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/195/60/001/001/003/007
B015/B060

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

SUBMITTED: January 4, 1960

Card 3/3

88359
S/195/60/001/004/004/015
B017/B055

5.4300

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 the Gaseous Phase Under Comparable Conditions
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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/cm^3 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/cm^3. 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 CH_4 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 the Gaseous Phase Under Comparable Conditions

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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

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Card 3/3

EMANUEL, N.M.

80661
S/153/60/003/02/09/034
B011/B003

5.3200

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

TITLE: The Thermal and Radiolytic Oxidation of Methyl Oleate

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1960, Vol. 3, No. 2, pp. 265-271

TEXT: The authors studied the kinetics of the accumulation of products of the thermal and radiolytic oxidation of the methyl oleate by atmospheric oxygen at 50 - 120°. For this purpose a vessel was used which was analogous to that described in Ref. 10. The peroxide amount was determined iodometrically. The acids were determined by titration of the oxidate dissolved in neutral ethanol with an 0.05 N-solution of alcohol-alkali solution. An x-ray apparatus of type RUP 1-M-2, 200 kV was used as radiation source. Air was blown through at a rate of 5 - 7 l/h. The authors proved that the principal amount of the oxidation products is formed by conversion of the hydroperoxides (Refs. 1-4).

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A large amount of oxides was also found, however. The authors assume that in addition to peroxides, oxides represent primary oxidation products of the methyl oleate. Furthermore, the authors studied the decomposition kinetics of the organic peroxides in dependence on the oxidation time of the methyl oleate (Fig. 3). They determined that peroxides decompose after the reaction of second order. The constant of the decomposition rate decreases with the intensity of oxidation (Fig. 3). The authors pointed out that a short radiation effect on the oxidation process is mainly expressed by the reduction of the induction period of the peroxide-, acid-, and oxide formation. The reduction in the induction period is proportional to the radiation dose (Fig. 5) in the case of peroxides, but is independent of the radiation dose in the case of oxides. Finally, the authors proved that the amount of peroxide yield subject to radiation is largely dependent on temperature (Fig. 7). The elimination of the radiation source strongly affects the kinetics of the accumulation of peroxides at comparatively low temperatures. Above 80° this influence cannot be observed (Fig. 6). The authors thank Professor N. A. Bakh, and

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N. N. Sarayeva for having supplied the radiation source. There are 8 figures and 15 references, 6 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: August 4, 1958

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

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 $2.8.10^{-9}$ 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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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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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

EMANUEL', N. M.

86408
S/062/60/000/008/015/033/XX
B013/B055

5.3190 2209, 1208, 1274

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

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

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

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

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

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

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

SUBMITTED: February 18, 1959

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82689

S/062/60/000/008/002/012
B004/B054

5.4300

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

TITLE: Macroscopic Stages in the Reaction of Propane Oxidation in the Presence of Chlorine

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1342-1347

TEXT: Various investigations (Refs. 1-4), as well as papers by V. I. Urizko and M. V. Polyakov (Ref. 5), N. S. Yenikolopov and G. S. Konareva (Ref. 6), studied the kinetics of exothermic chain reactions by measuring the development of heat in the reaction mixture. The existence of two time-separated macroscopic stages was observed. The authors applied this method to study the course of propane oxidation. Fig. 1 shows the curves of heat development and pressure variation for the stoichiometric mixture $C_3H_8 + O_2$ at 340 and 358°C and 244 torr. The heat development shows a maximum. The linear course of the function $\log \Delta p = f(t)$ corresponds to Semenov's law on the initial stage of branched chain reactions. With addition of 2% by volume of chlorine, the character of heat development changes. Fig. 2

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shows the course of reaction at 327°C. There are two maxima, the first after 25 sec, the second after 600 sec. Figs. 3-5 show the course of reaction with different chlorine additions (3.5%, 8%) and temperatures (340, 358, 372°C). The existence of two maxima is explained by the course of two degenerate branched chain reactions. The authors give the following reaction diagram: $B + R \rightarrow C + R$ (1); $C \rightarrow 2R$ (2); $A + R' \rightarrow D + Q'$ (3); $D + C \rightarrow 2R'$ (4); $R \rightarrow$ loss (5); $R' \rightarrow$ loss (6), where B is the initiating admixture, A the initial substance, R and C the free radical and the end product of the first reaction, R' and D the free radical and the end product of the second reaction. The linear breaking-off of the reactions (5) and (6) is caused by the loss of radicals on the walls of the vessel. The authors write down the differential equations for the reaction rates, substitute the experimental data for concentration, as well as the constants, and obtain the kinetic curves Fig. 6 for B, C, and D by means of numerical integration. The equation $\Delta T_m = k(Q_1W_1 + Q_2W_2)$ is written down for the heat development, where Q_1, Q_2 denote the thermal effect of the first and second stage, respectively, $W_1 = -dB/dt$; $W_2 = dD/dt$; $k = R^2/4\lambda$ (R = radius of the reaction vessel, λ = mean heat conductivity of the reacting gases). Fig. 7 shows

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B004/B054

that this equation exhibits courses of reaction analogous to the experiments, dependent on the ratio of a_1/a_2. The authors thank D. G. Knorre for the discussion. There are 7 figures and 7 Soviet references.

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

SUBMITTED: January 28, 1959

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S/062/60/000/009/003/021
B023/B064

AUTHORS: Obukhova, L. K. and Emanuel', N. M.

TITLE: The Acid Composition in the Oxidation of n-Decane in the Liquid Phase

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 9, pp. 1544-1548

TEXT: The authors studied the qualitative composition of the acid mixtures and explain the quantitative kinetic laws of the behavior of individual acids formed in the course of n-decane oxidation. The apparatus, the conditions of experimenting, and the methods of determining the reaction products have been described in a previous paper (Ref. 1). Oxidation was carried out without catalyst in the oxygen current at 140°C. Special methods of isolating the fraction of free acids, as well as their analysis with respect to individual components were developed. The system N-butanol - water - acetic acid (40 ml : 50 ml : 2.5 ml) was used to separate the acid mixtures beginning with formic acid and ending with butyric acid, to separate the acid mixtures from C_5 to C_{10} the system

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The Acid Composition in the Oxidation of n-Decane in the Liquid Phase

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B023/B064

benzene - water - formic acid (1 : 1 : 1). An oxidizer amount, containing $10-15\cdot10^{-4}$ M acids, was sufficient to identify the components and determine them quantitatively. Special methods of determining were developed since it was possible for mixtures to contain also oxy- and ketoxy acids apart from monocarboxylic acids. These methods are described in the following. Fig. 3 shows the kinetic curves of the concentration of the main products of oxidation: peroxides, carbonyl compounds, alcohols, and acids. From the chromatograms (Figs. 1 and 2), it is concluded that the acid products chiefly consist of lowmolecular acids and acids of medium-molecular weight. Fig. 4 shows kinetic curves of the formation of individual acids. The analysis of the kinetic behavior of individual acids in the course of reaction, permits the following conclusion to be drawn: The kinetic character of the curve does not change with increasing transformation intensity, and does not depend on the molecular weight of the acid. Acids, from acetic to valeric acid result in practically equal quantities. Capronic acid (C_6) gives a somewhat smaller yield, C_7, however, forms only half the amount of all other acids. In the course of investigation, the amounts of acidsdo not change. The ratio between the keto-, oxy-, and

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The Acid Composition in the Oxidation of n-Decane in the Liquid Phase

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B023/B064

monocarboxylic acids remains unchanged in the course of the process. Oxy- and keto acids do never form more than 18% of the total acid quantity, forming during oxidation. A burning out of the higher acids was not found to exist in the oxidation process. In the authors' opinion, the acid distribution established by them is not in agreement with accepted notions. In conclusion, they point out that it would be necessary to study the mechanism of individual stages of the complex oxidation process, leading to the formation of the acids. There are 4 figures, 2 tables, and 9 references: 3 Soviet, 1 British, and 5 German.

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

SUBMITTED: May 5, 1959

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Card 3/3

BURLAKOVA, Ye.B.; DZANTIYEV, B.G.; ZEFIROVA, A.K.; SERGEYEV, G.B.;
EMANUEL', N.M.

Thermal and radiolytic oxidation of methyl oleate. Izv.vys.
ucheb.zav.; khim.i khim.tekh. 3 no.2:265-271 '60.
(MIRA 14:6)

1. Moskovskiy gosudarstvennyy universitet imeni M. V. Lomonosova,
kafedra khimicheskoy kinetiki.
(Oleic acid)

S/074/60/029/012/003/004
B013/B078

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

TITLE: Catalysis With Metals of Variable Valence in Oxidation Reactions in the Liquid Phase

PERIODICAL: Uspekhi khimii, 1960, Vol. 29, No. 12, pp. 1409 - 1438

TEXT: This is a survey of experimental data published over the past decade concerning oxidation processes in the liquid phase under the catalytic action of metals of variable valence. The review offers a broad outline of mechanisms by which the salt-catalysts act upon the oxidation of aldehydes and hydrocarbons. The existing experimental material concerning the catalytic oxidation of organic compounds (Refs.4-6, 8, 10, 16-49; Figs.1-6; Tables 1-3) indicates that catalysts of variable valence take an active part in the initiation of chains. The basic difference between these catalysts and the peroxides as well as azo compounds is that each molecule of the catalyst may repeatedly participate in the initiation of a chain by causing the transformation of molecular products into free radicals. The mechanism of the initiation of chains, however, has not been

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Catalysis With Metals of Variable Valence in Oxidation Reactions in the Liquid Phase

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B013/B078

investigated more closely. A further function of catalysts of variable valence, e.g., the tearing of chains has been examined in Refs.11, 20-23, 27, 38, 50-52. (Tables 7-11). Such a reaction takes place when the catalyst reacts with free radicals. The inhibiting effect of the catalysts is in most cases non-apparent due to the stronger acting effect of initiation. A thorough study of the inhibiting effect of catalysts is still in its initial stage. Physico-chemical properties of catalysts in hydrocarbon solutions were investigated in Refs.3, 5, 20-24, 43, 53-64 (Fig.12, Tables 4,5), where salt molecules were found to associate into micellas. About the dependence of oxidation rate on the concentration of the catalyst, opinions diverge. Just as with the oxidation of hydrocarbons in the gas phase in the presence of catalysts (Ref.65), also in the liquid phase in the presence of catalysts of variable valence the reaction course was observed to take place in successive macroscopic stages limited in time. (Refs.8, 7, 10, 59, 65, 55; Figs.13, 14). The causes of such a stepwise course could, up to now, only be explained in rough outlines. The study of the regulating action of the catalyst during oxidation is dealt with in Refs.10-12, 17, 21, 67-73 (Figs.15-20, Table 6). On the basis of existing experimental materials, the following may be stated on the

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Catalysis With Metals of Variable Valence in Oxidation Reactions in the Liquid Phase

S/074/60/029/012/003/004
B013/B078

catalytic effect of metal salts of variable valence: The effect of salt catalysts upon oxidation is complicated and has various aspects. The catalysts react with oxidation products such as hydroperoxides and aldehydes under formation of free radicals. At the same time, several catalysts react with free radicals under tearing of chains. Under certain conditions, such catalysts have an inhibiting action upon oxidation. Besides, salt catalysts contribute to the lengthening of chains and regulate the composition of the resulting oxidation products. While the catalysts have an effect on the process of oxidation, they undergo complicated physicochemical transformations in their turn. Products of the developing reaction, particularly acids, extract the catalyst in the precipitate, which causes the further course of reaction to take place under a weaker participation of the catalyst. In spite of the complicated mechanism of catalytic oxidation, a number of symptoms could be determined, the knowledge of which will undoubtedly help in working out rigorously controllable oxidation methods. Mention is made of V. K. Tsyskovskiy, N. A. Kiseleva, and B. G. Freydin. There are 20 figures, 6 tables, and 73 references: 31 Soviet.

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

5.3200

68994

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

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

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 $1.7 \cdot 10^{-3}$ 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 RO_2-radicals 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 $1.7 - 1.9 \cdot 10^{-3}$ 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. 4

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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81421

S/020/60/132/06/61/068
B011/B003

21.6300

AUTHORS: Sapezhinskiy, I. I., Emanuel', N. M., Corresponding Member AS USSR

TITLE: Energy Levels of Metastable States of Biological Objects and the Mechanism Underlying the Action of Certain Protective Substances Against Radiation 19

PERIODICAL: Doklady Akademii nauk SSSk, 1960, Vol. 132, No. 6, pp. 1441 - 1443

TEXT: In a previous paper (Ref. 1) the authors proved that γ-radiation produces metastable states in protein, ribonucleic acid (RNA), and desoxyribonucleic acid (DNA). These are similar to those formed by photoexcitation of the most important components of the cell. The authors studied the phosphorescence spectra (at 77°K) of several substances, and described the experiments with protein, DNA, and RNA. Further, they took spectra of homogenates of some organs of mice and the phosphorescence spectra of several protective substances against radiation. Fig.1 compares the spectra of a 1% solution of ovalbumin, a 0.01% solution of

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Energy Levels of Metastable States of Biological S/020/60/132/06/61/068
Objects and the Mechanism Underlying the Action B011/B003
of Certain Protective Substances Against Radiation

the ribonucleic acid of yeast, and of a 0.01% solution of DNA from the thymus of the calf. The agreement of the triplet levels of RNA and DNA with the two triplet levels of protein, liver, and milt homogenates might be of fundamental importance. This is indicative of a mutual energy transfer between protein and nucleic acids. The triplet level of DNA is the lowest in the system under review. For this reason, DNA is probably damaged by radiation if energy is transferred from other chemical components of the cell to DNA. Following this, the authors took spectra of 0.1% of aqueous solutions of the following protective substances against radiation: β-mercaptoethylamine, β-aminoethylisothiuronium, tryptamine, serotonine, histamine, epinine, propylgallate, and isopropylgallate (Table 1). It may be seen from Table 1 that wavelengths corresponding to the phosphorescence maxima of DNA, the protective substances against radiation, and the propyl esters of gallic acid are in close agreement with one another. The energy transfer from triplet levels of DNA to the triplet levels of the protective substances is very likely in this case. Therefore, the damage of DNA must be considerably reduced. One molecule of the protective substance passes from

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Energy Levels of Metastable States of Biological S/020/60/132/06/61/068
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the singlet level to the triplet level. The interrelation between the energy levels of protein, RNA, DNA, and one of the protective substances (β-mercaptoethylamine) is schematically shown in Fig. 2. The mechanism underlying the action of inhibitors of free radical reactions must be studied further. This mechanism may be regarded as an interaction between free valences of the biradical and the inhibitors. Consequently, a small amount of active radicals of the inhibitor might form. If propylgallate is introduced into a protein solution, the lifetime τ of the metastable states is considerably reduced. The protein loses its phosphorescence, and τ is shortened by one-half or one-third. There are 2 figures, 1 table, and 6 references: 3 Soviet, 1 Swiss, and 1 German.

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

SUBMITTED: February 16, 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: $RO_2^{\cdot} \longrightarrow R'O^{\cdot} + R''OH$ (1) and $RO_2^{\cdot} + RH \longrightarrow RO_2H + R^{\cdot}$ (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 S/020/60/133/01/40/070
Alcohol in the Liquid and in the Gaseous Phase 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 Phase

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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

4

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 Jl '60.
(MIRA 13:7)

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

EMANUEL', N.M.; GORBACHEVA, L.B.; SOKOLOVA, I.S.

Inhibition of protein synthesis in Ioshida ascitic hepatoma cells by substances inhibiting free-radical prodesses. Dokl. AN SSSR 134 no.6:1475-1477 O '60. (MIRA 13:10)

1. Institut khimicheskoy fiziki Akademii nauk SSSR. 2. Chlen-korrespondent AN SSSR (for Emanuel').
(TUMORS) (PROTEIN METABOLISM) (GALLIC ACID)

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

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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 $8.2\cdot10^{-7}$ and $3.3\cdot10^{-7}$ mole/l, the oxidation of n-decane is nearly entirely inhibited. If the α-naphthol content drops from $3.3\cdot10^{-7}$ to $3.1\cdot10^{-7}$, 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.

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

SUBMITTED: July 22, 1960

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86040

21.6300

S/020/60/135/003/024/039
B016/B054

AUTHORS: Burlakova, Ye. B. and Emanuel', N. M., Corresponding Member AS USSR

TITLE: Characteristics of the Effect of Mercamine and of Inhibitors of Radical Chain Processes in Reactions Simulating the Oxidation of Lipins

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 135, No. 3, pp. 599 - 602

TEXT: The authors report on a comparison between known preservatives against the radiation disease (mercamine) and inhibitors of radical chain reactions (hydroquinone) with respect to their effect on the oxidation of methyl oleate. The latter was taken as simulating system for the lipin oxidation. The authors classify prophylactic and curative inhibitors as follows: 1) Inhibitors of radical chain processes reacting with radicals of the $R^{\cdot}$-type according to the scheme: $R^{\cdot} + HIn \longrightarrow RH + In^{\cdot}$; 2) inhibitors reacting with $RO_2^{\cdot}$-radicals according to the scheme: $RO_2 + HIn \longrightarrow ROOH + In^{\cdot}$ (where HIn is the inhibitor, $In^{\cdot}$ a poorly active radical); 3) substances

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Characteristics of the Effect of Mercamine S/020/60/135/003/024/039
and of Inhibitors of Radical Chain Processes B016/B054
in Reactions Simulating the Oxidation of Lipins

destroying peroxides. The authors' data concerning the irradiation of inhibited methyl oleate in the presence or absence of oxygen confirm the opinion (Ref. 6) that hydroquinone is mainly consumed by the reaction with RO_2-radicals. Hydroquinone introduced before the reaction begins inhibits the formation of primary oxidation products of methyl oleate i.e. of peroxides and oxides; besides, hydroquinone prolongs the induction period. If hydroquinone is introduced in a reacting system, it inhibits the formation of peroxides, but not their decomposition. Consequently, the content of peroxides is slightly reduced (Fig. 2). Hence, the authors conclude that peroxides undergo a chain-like decomposition process. As mercamine is a good reducing agent, the authors assumed that it would readily react with peroxides. This was confirmed by introducing mercamine in a reacting system with a considerable peroxide amount. The authors assume that mercamine in the reaction with peroxides is transformed into sulfonic derivatives since the quantity of mercamine introduced amounted to only 1/2 - 1/3 of the destroyed peroxides. The authors had proved earlier (Ref. 4) that oxides form in methyl oleate irrespective of and parallel with peroxides. In the authors' opinion, they are formed by free-radical

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Characteristics of the Effect of Mercamine S/020/60/135/003/024/039
and of Inhibitors of Radical Chain Processes B016/B054
in Reactions Simulating the Oxidation of Lipins

reactions. In their further investigation of the effect of mercamine as a weak inhibitor of the "radical" type, the authors studied the common effect of a mercamine - hydroquinone mixture. They arrived at the conclusion that mercamine - besides its effect as a weak inhibitor - acts by the mechanism of peroxide destruction, and is an efficient synergist of inhibitors reacting with radicals. The authors found that the synergy $\Delta\tau_{syn}$ (difference between the induction period $\tau_{mixture}$, caused by the inhibitor mixture, and the sum $\tau_{hydroqu} + \tau_{merc}$) is much more dependent on the amount of mercamine introduced than on the amount of hydroquinone. On the premise that the mechanism of this effect is based on the reduction of oxidized hydroquinone (e.g. of the semiquinone radical), the authors interpret the result obtained as follows: The amount of the reacting radical inhibitor (which is more efficient than mercamine) is, as it were, increased by the reduction mentioned. The authors explain the protective action of mercamine by its properties which destroy peroxides and reduce oxidized inhibitors. Mercamine protects the tissue inhibitors from

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Characteristics of the Effect of Mercamine and of Inhibitors of Radical Chain Processes in Reactions Simulating the Oxidation of Lipins

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B016/B054

destruction by radiation, and preserves their specific effect. Finally, the authors state that inhibitors destroying the R˙-radicals (inhibitor type 1) are required to prevent the radiation disease. If the tissue inhibitors are already destroyed, substances of the mercamine type may be insufficient. For a comprehensive therapy, peroxide-destroying inhibitors should be used besides the radical inhibitors. There are 2 figures and 7 references: 6 Soviet and 1 US.

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

SUBMITTED: August 2, 1960

Card 4/4

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EMANYEL', N.M.; LYASKOVSKAYA, Yu.N., kand. tekhn. nauk; PETROV, N.A., kand. tekhn.nauk, spets. red.; BELIKOVA, L.S., red.; KISINA, Ye.I., tekhn. red.

[Inhibition of the oxidation of fats] Tormozhenie protsessov okisleniia zhirov. Moskva, Pishchepromizdat, 1961. 358 p. (MIRA 14:9)

1. Chlen-korrespondent AN SSSR (for Emanyel').
(Oils and fats) (Oxidation)

EMANUEL, N. M. (USSR)

"Specific Inhibition of Redox Enzymes by Inhibitors for Free-radical Processes."

Report presented at the 5th International Biochemistry Congress, Moscow, 10-16 Aug 1961

EMANUE~~R~~L, N.M., GORBACHEVA, L.B. (USSR)

"Suppression of Cell Protein Biosynthesis in Yoshida Ascites Hepatoma by Free-Radical Reaction Inhibitors."

Report presented at the 5th Int'l. Biochemistry Congress, Moscow, 10-16 Aug. 1961.

S/081/62/000/003/019/090
B151/B144

AUTHORS: Obukhova, L. K., Emanuel', N. M.

TITLE: Mechanism of formation of acids in the liquid-phase oxidation of n-alkanes

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 3, 1962, 72, abstract 3B479 (Tr. po khimii i khim. tekhnol. (Gor'kiy), no. 1, 1961, 132-138)

TEXT: Using chromatographic analysis the constitution of the mixtures of acids formed in the liquid-phase oxidation of n-decane is established. The majority of the acids is made up of low-molecular acids from acetic to valerianic acids. Capronic and enanthic acids are formed in smaller quantities. C_8, C_9, and C_{10} acids are present only as traces. The quantitative relationship between the acids is not changed during oxidation. Additions of caprylic acid to decane during oxidation has shown that higher acids are practically unconsumed during oxidation. To clarify the mechanism of formation of acids from ketones the oxidation of undecanone-6 is used. Among the products of oxidation, peroxides were

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Mechanism of formation of acids...

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B151/B144

found along with the acids and lactones. The γ-lactones are identified using infrared spectra. A hypothesis is put forward on the formation of acids and lactones from the isomerization and subsequent decomposition of the keto-peroxide radical. This hypothesis gives a qualitative explanation of the preponderance of low-molecular acids in the products from oxidation of n-decane. [Abstracter's note: Complete translation.]

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S/081/62/000/005/008/112
B158/B110

AUTHOR: Emanuel', N. M.

TITLE: Critical effects in slow degenerate branching chain reactions of hydrocarbon oxidation in liquid phase

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 5, 1962, 59, abstract 5B381 (Tr. po khimii i khim. tekhnol. (Gor'kiy), no. 1, 1961, 208 - 215)

TEXT: This is a report given at a Symposium on homolytical reactions in liquid phase. The most characteristic feature of branching chain reactions is the presence of critical effects, i. e. extremely abrupt changes in the reaction velocity with negligible changes in one of the parameters characterizing the course of the process (pressure, temperature, concentration of reactants). An examination is made of the effect of critical concentration of copper stearate during oxidation of n-decane (RZhKhim., 1959, no.24, 85348), the effect of critical concentration of the classic inhibitor - α naphthol - in the same reaction (RZhKhim., 1961, 13B508),

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S/081/62/000/005/008/112
Critical effects in slow degenerate... B158/B110

and the effect of critical concentration of a solvent (benzene) in the oxidation of liquefied butane (Abstract 5B382). [Abstracter's note: Complete translation.]

Card 2/2

OBUKHOVA, L.K.; BOLDIN, A.A.; EMANUEL', N.M.

Mechanism of the liquid phase oxidation of aliphatic ketones.
Neftekhimiia 1 no.1:70-73 Ja-F '61. (MIRA 15:2)

1. Institut khimicheskoy fiziki.
(Ketones) (Oxidation)

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

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

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

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

5.1190 2209 1297 1274

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

TITLE: Catalytic decomposition of ethyl benzene hydroperoxide

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

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

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

Catalytic decomposition of...

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

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Catalytic decomposition of...

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B118/B208

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

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

SUBMITTED: April 4, 1960

Card 3/3

BLYUMBERG, E.A.; ZAIKOV, G.Ye.; EMANUEL', N.M.

Gas- and liquid phase oxidation of n-butane. Neftekhimiia 1 no.2:235-243 Mr-Ap '61. (MIRA 15:2)

1. Institut khimicheskoy fiziki AN SSSR.
(Butane)
(Oxidation)

33588

S/204/61/001/005/006/008
E075/E484

11.0132

AUTHORS: Obukhova, L.K., Gol'dberg, V.M., Kozlova, Z.G., Emanuel', N.M.

TITLE: Oxidation of liquid hydrocarbons with high degree of conversion

PERIODICAL: Neftekhimiya, v.1, no.5, 1961, 669-674

TEXT: The object of this work was to study oxidation of n-decane with continuous removal of water forming during the reaction. The removal of water and, with it, a part of low-boiling point acids, such as formic and acetic acids, greatly affects the speed of oxidation. Kinetic curves for the formation of acids at 160, 150, 140 and 130°C under conditions of water removal (curves 1, 2, 3 and 4) are given in Fig.1. The formation of acids, carbonyl compounds and CO_2 is autocatalytic. Kinetic curves for the formation of alcohols have a definite maximum. The curves of this type indicate that the alcohols are intermediate products in the oxidation reaction. The large quantity of CO_2 formed during the reaction indicates that there are processes leading to the destruction of the hydrocarbon skeleton of molecules. Whilst the

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Oxidation of liquid hydrocarbons ... E075/E484

content of alcohols in the reaction mixture rapidly passes through a maximum (5 to 6% mole), ketones accumulate in considerable quantities (up to 20% mole) and the kinetic curves do not show a maximum. It is noticeable that the greater velocities of formation of acids and CO_2, after the initial period of acceleration is finished, remain constant for a long time and do not depend on the degree of oxidation of the hydrocarbons. Energy of activation was found to be 28 kcal for the formation of CO_2, acids and conversion of n-decane. It is concluded that CO_2 formed is not a product of further oxidation and destruction of acids but forms simultaneously with an acid molecule. The experiments confirm that the retarding effect of water is connected with the formation of complexes of the hydroxyl radical with RO_2, but another possible effect is the cooling action exerted by the water of reaction which is not soluble in the reaction mixture and evaporates. This may lower the temperature of the mixture by about 20°C, which for activation energies of ca 30 kcal may give a tenfold reduction of the reaction velocity. Moreover, the complex formation between RO_2 and HOH, which also reduces the

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Oxidation of liquid hydrocarbons ... S/204/61/001/005/006/008
E075/E484

reaction velocity, is more pronounced at lower temperatures. The removal of formic and acetic acids may prevent the process of decomposition of hydroperoxides into ions RO^- and OH^-, thus preventing their participation in the chain reaction. The results obtained show however that after the removal of water and light acids the decomposition of hydroperoxides proceeds at the same rate as it does in the presence of water. V.K.Tsyskovskiy is mentioned in the article in connection with his contributions in this field. There are 6 figures and 11 references: 10 Soviet-bloc and 1 non-Soviet-bloc.

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

SUBMITTED: October 2, 1961

Card 3/3

EMANUEL', N.M.

S/1[illegible]/61/002/004/006/008
E111/E585

AUTHORS: Mayzus, Z.K., Skibida, I.P. and Emanuel', N.M.

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

PERIODICAL: 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 studied, together with Ye. T. Denisov (Ref.7: Dokl. AN SSSR, 128, 755, 1959), an 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 pure decane was added at a constant rate, the volume of liquid in the vessel being kept constant by continuous removal through tube 2

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(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 1.25 hour^{-1}. Samples, taken periodically, were analyzed for hydroperoxides, alcohols, ketones and acids. For a given temperature and addition rate there can be only one stationary state. Fig.4 shows concentrations of a) alcohols, б) ketones and в) acids, respectively, as functions of time (hours) for various values of v. The numbers on the curves correspond to the various values of v: 1 - v = 0.935; 2 - v = 0.625; 3 - v = 0.312; 4 - v = 0.156; 5 - v = 0.0935. The authors analyse the mathematical relations between these curves and the curves of stationary concentrations of acids C_K and hyperperoxides C_r as functions of v (curves 1 and 2, respectively, Fig.5; ordinates are in mol/litre). Both "false start" and "overshoot" types of kinetic curves were found. From their considerations of all the factors they conclude that these effects can occur, for a succession $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, independently of the relative values of k_1 and k_2. Representing the concentrations of A and B by x and y.

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

$$v < \frac{k_1 \Delta x_o}{\Delta y_o} - k_2$$

with $\Delta x_o > 0$ and $\Delta y_o > 0$ or $\Delta x_o < 0$ and $\Delta y_o < 0$. Here $\Delta x_o = x_o - \bar{x}$ and $\Delta y_o = y_o - \bar{y}$. "Overshoot" can occur at all the values of v if $\Delta x_o > 0$, $\Delta y_o < 0$ or $\Delta x_o < 0$ and $\Delta y_o > 0$. The sign of the differential $(d\Delta y/dt)_{t=t_o}$ is determined only by the sign of Δx_o. 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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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)

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KNORRE, V.L.; EMANUEL', N.M.

Kinetics of 1,2-diphenylethane oxidation with potassium permanganate in aqueous solutions. Kin.i kat. 2 no.6:816-820 N-D '61. (MIRA 14:12)

1. Institut khimicheskoy fiziki AN SSSR.

(Ethane)
(Potassium permanganate)

EMANUEL N.M.

5.4600

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E134/E485

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

TITLE: The effect of gamma radiation on the oxidation of methyl oleate in the presence of inhibitors of free radical processes

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy SSSR. Khimiya i khimicheskaya tekhnologiya, v.4, no.5, 1961, 751-754

TEXT: In previous work on the radiological oxidation of natural fats (Ref.1: Izv. VUZ SSSR. Khimiya i khim. tekhnologiya, v.2, 533 (1959)), the present authors had related a reduced induction period with destruction of inhibitors by radiation. In view of the complexity of natural fats, in which the quantity and structure of antioxidants is unknown, the authors decided to study methyl oleate - inhibitor systems. Diphenylamine and hydroquinone, both known as inhibitors of free radical reactions, were employed. The authors had previously (Ref.2: Izv. VUS SSSR. Khimiya i khim. tekhnologiya, v.3, 265 (1960)) studied the effect of radiation on inhibitor free methyl oleate, and considered that radiation leading

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to free radical formation would destroy the inhibitors by reaction with free radicals. Samples were exposed to gamma radiation from Cobalt 60 in apparatus ГУТ-400 (GUT-400) and the destruction of the inhibitor was followed spectrophotometrically. Irradiation took place at 20°C. Oxidation experiments on irradiated and non-irradiated methyl oleate were carried out at 80°C with continuous passage of air. Experiments with inhibitor free methyl oleate were carried out simultaneously under identical conditions to obtain the rate of free radical formation. Experimental details and methods of analysis were as described in Ref.2. Curves showing the rate of free radical formation in inhibited and non-inhibited methyl oleate were found to be parallel and differed only in their induction period. The total induction period consists of the basic induction period for the oxidation of inhibitor free methyl oleate and an additional induction period related to the concentration of inhibitor; the latter is practically completely destroyed before free peroxide radicals are observed. The additional induction period is directly proportional to inhibitor concentration, which is characteristic of inhibitors reacting with radicals. Induction periods for

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The effect of gamma radiation ... irradiated material were lower than for non-irradiated material due to inhibitor destruction, and the decrease in induction period was found to be proportional to the quantity of radiation. Curves showing the relation between inhibitor concentration and induction period, and the decrease in induction period of inhibited methyl oleate with total quantity of radiation, are given as well as correlating equations. It has been shown that quantity of radiation is controlling, and that intensity has virtually no effect. At the low temperature of radiation, the induction period of non-inhibited methyl oleate was practically unaffected by radiation. The correlation between the induction period of inhibited methyl oleate and the quantity of radiation made it possible to calculate the number of radicals formed per unit of radiation. Experiments, carried out in the presence and absence of oxygen respectively, lead to the suggestion that removal of a hydroquinone type inhibitor takes place essentially by reaction with an RO_2 type radical. There are 5 figures, 1 table and 3 Soviet-bloc references.

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The effect of gamma radiation ...

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

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