

Photochemical oxidation of hydrogen. II. The reaction at high temperatures. A. B. Nalbandyan (Int. Chem. Phys. Acad. Sci. U.S.S.R., Moscow). *J. Phys. Chem. (U.S.S.R.)* 20, 1249-72 (1946) (in Russian); *Ch. C.A.* 34, 2710. — Mixts. of 2 H<sub>2</sub> + O<sub>2</sub> in a quartz tube were irradiated by a H discharge lamp. The rate of formation of H<sub>2</sub>O increased with the total pressure  $p$  (2-28 mm. Hg) at 20-348°, and showed a max. at  $p = 1$  mm. at higher temp. (368-383°). At 393° ignition took place between 7 and 12 mm. Hg. Above 370° the photochem. reaction is complicated by the dark reaction, the rate of which increases linearly with temp. At a const. pressure (20 mm.) the ignition temp. in the darkness is 118°, and is lowered by the strongest illumination used to 391°. Near the ignition limit,  $\nu$  increases with temp. and the intensity of irradiation  $I$ , and from these data the length of chains can be calcd. Below 380° this length is independent of  $I$  and equal to 2.4. Above 380° it is greater, the greater  $I$ . The max. length of chain achieved before ignition takes place is 11 at the smallest, and 6 at the greatest  $I$  used. The very long chains postulated by Semenova (*C.A.* 31, 7728) near the ignition limit could not be detected. The effect of temp. and  $I$  on the chain length is in agreement with the mechanism postulated by Lewis and Elbe, *Combustion, Flames and Explosions of Gases* (*C.A.* 32, 4787). III. A theory of the interaction of chains. *Ibid.* 1273-82 (in Russian). — The lowering of the ignition temp.  $T$  by irradiation cannot be explained by the thermal effects of the irradiation because calcn. shows these effects to be very small. A correct interpretation is given by supplementing the reaction mechanism postulated by Lewis and Elbe (*loc. cit.*) with the reaction  $HO_2 + HO_2 = H_2O + O_2 + O$  in which 2 relatively inert radicals produce a new active atom. Then the rate of reaction depends on the original number,  $n_0$ , of active centers. Irradiation lowers  $T$  because it creates new active centers, i.e., increases  $n_0$ . If the coll. of interaction of 2 chains is  $p$ , the ignition takes place when  $\rho n_0 = 1$ . The value of  $n_0$  created by irradiation is calcd. from the rate of the photochem. oxidation of H<sub>2</sub> at room temp. when the chain length is 1. From this value and the condition  $\rho n_0 = 1$  at ignition, the lowering of  $T$  and the chain length at various irradiations are calcd. in agreement with the exptl. data. J. J. Bikerman

Precis available.  
W 64/49 26 Jan 49



NALBANDYAN, A.B.

Measurement of the quantum yield in the oxidation of methane,  
sensitized by mercury. Dokl. AN Arm. SSR 9 no.3:101-103 '48.  
(MLRA 9:10)

1. Institut khimicheskoy fiziki Akademii nauk SSSR, Khimichskiy  
insitut Akademii nauk Armyanskoy SSR, Moskva-Yerevan. Predstavleno  
I.I. Semenovym.

(Methane) (Oxidation)

NALBANDYAN, A. B.

PA 56/49T22

USSR/Chemistry - Photochemical Reactions      Dec 48  
Chemistry - Oxidation

"Mechanism of the Photochemical Oxidation of Methane,"  
A. B. Nalbandyan, Lab of Kinetics of Photochem  
Reactions, Inst of Chem Phys, Acad Sci USSR, Moscow,  
10 $\frac{1}{2}$  pp

"Zhur Fiz Khim" Vol XXII, No 12

Discusses (1) experiments under fixed conditions,  
(2) quantum output of the reaction, and (3) research  
on intermediate products of the reaction under dynamic  
conditions. Submitted 22 Apr 48.

56/49T22



PROCESSES AND PROPERTIES

2

CA

Nalbandyan, A. B., and Voevodskii, V. V.: Mekhanizm  
 Oksidatsiya i Goreniya Vodoroda (Mechanism of the  
 Oxidation and Combustion of Hydrogen). Moscow-  
 Leningrad: Inst. Khim. Fiz. Instatel. Akad. Nauk S.S.S.R.,  
 1949. RD. Reviewed in *Uspekhi Khim.* 18, 376(1949).

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

SIGNI ROMIIV

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100
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NALBANDYAN, A.B. (Editor)

A compendium of work on kinetics of oxidation chain reactions, including oxidation of oxygen, mechanism of low temperature oxidation of carbon oxide, etc; published by the Academy of Sciences, USSR. i gorenia vodoroda The machinery for the oxidation and combustion of hydrogen. Moskva, Izd-vo Akademii nauk SSSR, 1949. 178 p. (52-28543)

QD 181. HLN2

NALBANDYAN, A.B. & V. V. VOEVODSKII

RT-1158 (The process of oxidation and combustion of hydrogen) Preface, Chapters I and II  
(pp.) 3-41) of:  
MEKHANIZM OKISLENIIA I GORENIIA VODORODA Moscow-Leningrad, 1949.



NALBANDYAN, A. B.

"Mechanism of Photochemical Oxidation of Ethane Sensitized by Mercury," Vest. Ak. Nauk, No. 6, June, 1949. Discusses new methods of microelementary analysis developed in the Laboratory of Quantitative Microanalysis, Institute of Organic Chemistry, Acad. of Sci.

PA 54/47114

NAIBANDYAN, A. B.

USSR/Chemistry - Chemical Sciences  
Academy of Sciences

Jun 49

"In the Department of Chemical Sciences" 6 pp

"Vest Ak Nauk SSSR" No 6

Following reports submitted: A. V. Kirsanov's  
"Conversion of Carboxylic Acids Into Amides," A. B.  
Naibandyan's "Mechanism of Photochemical Oxidation  
of Ethane Sensitized by Mercury," A. I. Brodskiy's  
"Mechanism of Allylphenyl Regrouping and the Struc-  
ture of the Hydrogen Bond in Benzoguinhydrone," and  
A. V. Trofimov's "Composition of Meteoritic and  
Earth Sulfure." *Discussion on methods of  
microelementary analysis developed in Lab of  
Quantitative Microanal, Inst of Org Chem.*

54/49714

PROCESSES AND PROPERTIES INDEX

3

*Ch*

**Mercury-sensitized photochemical oxidation of ethane. Investigation of the products.** A. B. Nalbandyan. *Doklady Akad. Nauk S.S.S.R.* 66, 413-10(1949). - In a flowing mixt. of 10% C<sub>2</sub>H<sub>6</sub> + 10% O<sub>2</sub>, satd. with Hg vapor at 80° and exposed to a quartz Hg lamp the products, at 300" and 50 mm. Hg, are a function of the flow velocity  $v$ . At the lowest  $v = 0.81$  cc./min., the products were 8.1 cc. aldehydes, 29 cc. CO, and 12.3 cc. CO<sub>2</sub>. The yields of CO<sub>2</sub> and of CO fall very fast with increasing  $v$ , CO<sub>2</sub> disappearing altogether at about  $v = 0$ , CO at 13 cc./min. The yield of aldehydes first increases somewhat with  $v$  at very low  $v$ , then, after passing through a max., decreases continually with further increasing  $v$ , down to 1 vol. % of the C<sub>2</sub>H<sub>6</sub> passed at  $v = 42$  cc./min. The ratio of HCHO to AcHl remains approx. const.  $\approx 5$ , independently of  $v$ ; thus, for 22 cc. passed the unts. of HCHO and AcHl, detd. polarographically, were, at  $v = 1.81, 7.25$  and 13 cc./min., resp. 2 and 0.30, 1.02 and 0.25, 0.24 and 0.5 cc. It indicates that, of the 2 reactions, C<sub>2</sub>H<sub>6</sub> + Hg(P<sub>1</sub>)  $\rightarrow$  2 CH<sub>3</sub> + Hg(S<sub>1</sub>) and C<sub>2</sub>H<sub>6</sub> + Hg(P<sub>2</sub>)  $\rightarrow$  C<sub>2</sub>H<sub>5</sub> + H + Hg(S<sub>2</sub>), the first is the easier one. In terms of the time of stay  $\tau$  in the irradiated zone, the amt. of C<sub>2</sub>H<sub>6</sub> consumed is represented by a straight line; the amt. of aldehydes produced coincides exactly with that of the C<sub>2</sub>H<sub>6</sub> reacted at about  $\tau = 0.35-2$  sec., but then it levels off to a value very nearly const., while the half-sum of CO + CO<sub>2</sub>, starting from zero at  $\tau = 2$  sec., rises very nearly linearly with  $\tau$ .

It is thus evident that CO and CO<sub>2</sub> are secondary products of decompn. of the primarily formed aldehydes. The chain nature of the reaction is demonstrated by the increase of the amt. of aldehydes with the temp., thus, at  $\tau = 0.82$  sec., for 238 cc. C<sub>2</sub>H<sub>6</sub> passed, the unts. of aldehydes at 25, 100, and 310° were 0.08, 1.23, and 3.80 cc., resp. At const. time of illumination, the yield of aldehydes is proportional to the square root of the intensity, consequently, termination of the chains occurs through recombination of the chain carriers in the vol. Presence of org. peroxides was detected; their amt. decreases very nearly linearly with increasing  $v$ ; thus, at 310°, for 651 cc. C<sub>2</sub>H<sub>6</sub> passed, at  $v = 9, 102$ , and 210 cc./min., the no. of mols. of peroxides formed was, resp., 4.9, 3.1, and  $2.9 \times 10^{18}$ , whereas the no. of aldehyde mols. decreased more nearly exponentially,  $8.1 \times 10^{19}$ ,  $7.1 \times 10^{19}$ , and  $1.8 \times 10^{19}$ . With increasing  $v$ , the ratio of peroxides to aldehydes increases. At very high  $v$ , i.e., very short  $\tau$ , peroxides should become the only intermediate products, to the exclusion of aldehydes. The reaction appears to proceed over org. radicals, forming peroxides thereof with O<sub>2</sub> and then stable peroxides with C<sub>2</sub>H<sub>6</sub>; the stable peroxides decomp. into aldehydes which, at sufficiently long  $\tau$ , give CO and CO<sub>2</sub>.

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METALLURGICAL LITERATURE CLASSIFICATION

FROM 80-117

BRIEF Des Des 111

BRIEF Des Des 111

NALBANDYAN, A., B.,

Pa. 150113

USSR/Chemistry - Photochemistry  
Oxidation

21 Jul 49

"Mechanism of Mercury-Sensitized Oxidation of Propane," N. V. Fok, B. B. Bereslavskiy, A. B. Nalbandyan, V. Ya. Shtern, Inst of Chem Phys, Acad Sci USSR, 3 pp

"Dok Ak Nauk SSSR" Vol LXVII, No 3

Formerly, high temperature necessary for photochemical oxidation of methane and ethane prevented any substantial yield of peroxides and aldehydes. Here, yield of these products was studied as a function of time of exposure in photochemical oxidation of propane in temperature interval 20 - 300° C at a pressure of 50 mm of Hg. Results show peroxides are a primary intermediate product (with respect to temperature), while aldehydes are a secondary intermediate product. Submitted by Acad N. N. Semenov 16 May 49

Pa. 150113

NALBANDYAN, A. B.

USSR/Chemistry - Fuels  
Reaction Kinetics

Aug 52

"Investigation of the Composition of Peroxides Formed  
in the Oxidation of Propane at Room Temperature With  
Photochemically Sensitized Mercury," N. V. Fok and  
A. B. Nalbandyan

"DAN SSSR" Vol 85, No 5, pp 1093-1095

On the basis of chem and polarographic analysis and  
through the reaction of the peroxide with various  
substances, it was established that the peroxide  
formed during the oxidation of propane with photo-  
chemically sensitized Hg at room temp is isopropyl  
hydrogen peroxide. Submitted by Acad N. N. Semenov  
23 May 52.

239T27

NALBANDYAN A. B.

238T14

USSR/Chemistry - Fuels  
Combustion

Aug 52

"Periodic Combustion Flashes in Mixtures of Carbon Monoxide and Oxygen," N. S. Yenikolopyan and A. B. Nalbandyan

"DAN SSSR" Vol 85, No 6, pp 1309-1312

A quant description of the combustion observed in a mixt of CO and O2 when a small amount of H is added by diffusion is worked out on the basis of the reaction mechanism and the consts of elementary reactions calcd from previous work.

238T14

When the pressure of the H on the membrane is decreased and its rate of entry to the mixt is decreased, the time between explosions is increased. By means of eqs derived from the mechanism of the reaction, the article explains why the combustion is only a flash and not a complete burning of the entire mixt. Presented by Acad N. N. Semenov 14 Jun 52

238T14

NALBANDYAN, A. B.

PA 247717

USSR/Chemistry - Fuels, Peroxides 21 Sep 52

"The Mechanism of the Reaction of the Oxidation of Propane With Photochemically Sensitized Mercury at Room Temperature," N. V. Fok and A. B. Nalbandyan

DAN SSSR, Vol 86, No 3, pp 589-592

Propane is oxidized at room temp with photochemically sensitized Hg to form propyl hydrogen peroxide. The reaction proceeds with a preliminary excitation of the propane mol. Presented by Acad. N. N. Semenov 5 Jun 52

Nuclear Sci. Abs.  
1-31-54.

247717

*Handwritten:* M. B. ...

*Printed:* ...  
peroxide ...  
aged lamp for ...  
formation is lower function of light intensity, rate is not  
influenced by inert gas dilution. Concluded that peroxide  
radicals, destroyed on vessel walls, are main reaction centers

*Handwritten:* V B



Nalbandyan, A.B.

✓ The photochemical oxidation of propane at high temperatures. N. V. Fok and A. B. Nalbandyan. *Doklady Akad. Nauk S.S.S.R.* 89, 125-7(1953). 62. — The photochem. oxidation of  $C_3H_8$  was carried at 100–300°, for equal mixts. of  $C_3H_8$  and  $O_2$  at a pressure of 60 mm. At 160°  $AcH$  is present in the reaction products. At 200°, along with isopropyl hydroperoxide and  $AcH$ , formaldehyde is present in the reaction products to almost the same extent as  $AcH$ . As the temp. is further increased, the ratio of formaldehyde to  $AcH$  increases. Among the oxidation products at 300° are acetone and  $CO$ . The exptl. results indicate that the active centers for the photochem. reaction are the peroxide radicals which perish on the walls of the reaction vessel.

J. Rovtar Leach

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MALBANDYAN, A.P.

The Committee on Stalin Prizes (of the Council of Ministers USSR) in the fields of science and inventions announces that the following scientific works, popular scientific books, and textbooks have been submitted for competition for Stalin Prizes for the years 1952 and 1953. (Sovetskaya Kultura, Moscow, No. 22-40, 20 Feb - 3 Apr 1954)

<u>Name</u>	<u>Title of Work</u>	<u>Submitted by</u>
Malbandyan, A.P. Voyevodskiy, V.V.	"The Mechanism of the Oxidation and Combustion of Hydrogen"	Institute of Chemical Physics, Academy of Sciences USSR

SO: W-30604, 7 July 1954

*HALBANDYAN V.M. 1955*

HALBANDYAN, A.B., professor, redaktor; EMANUEL', N.M., professor, redaktor;  
CHEKEDNICHENKO, V.M., redaktor; ZELENKOVA, Ye.V., tekhnicheskij redak-  
tor

[Chain reaction of gaseous phase oxidation of hydrocarbons] TSepnye  
reaktsii okisleniya uglevodorodov v gazovoi faze. Moskva, 1955. 209 p.  
(MLRA 9:1)

1. Akademiya nauk SSSR. Institut khimicheskoy fiziki  
(Hydrocarbons) (Oxidation)

*Nalbandyan A.B.*

USSR/Kinetics - Combustion. Explosions. Topochemistry. Catalysis. B-9

Abs Jour : Referat Zhur - Khimiya, No 6, 1957, 18562

Author : N.V. Fok, A.B. Nalbandyan.

Inst : Academy of Sciences of USSR.

Title : To Mechanism of Photochemical Oxidation of Hydrocarbons.

Orig Pub : in the symposium Tsepnyye reaktsii okisleniya uglevodoro-  
dov v gazovoy fatsii. M., AN SSSR, 1955, 118-139.

Abstract : Review of works published by the authors earlier  
(Nalbandyan A.B., Zh. fiz. khimii, 1948, 22, 1443; Dokl.  
AN SSSR, 1949, 66, 473; Fok N.V., Bereslavskiy B.B., Nal-  
bandyan A.B., Shtern V.Ya., Dokl. AN SSSR, 1949, 67, 499;  
Fok N.V., Nalbandyan A.B., Dokl. AN SSSR, 1952, 85, 1093;  
86, 589; RZhKhim, 1953, 2853).

Card 1/1

- 233 -

Investigation by use of laboratory methods of the following:

*MR. PATTON*

NALBANDYAN, H. B.

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

B-9

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 11220

Author : Kleyenov N.A., Antopova I.N., Markovich A.N., Nalbandyan A.B.

Title : Oxidation of Methane by Oxygen Atoms Formed on Thermal Decomposition  
of Ozone

Orig Pub : Zh. fiz. khimii, 1956, 30, No 4, 794-797

Abstract : Formation of peroxide on oxidation of  $\text{CH}_4$  under conditions of flow  
(mixture  $\text{CH}_4 : \text{O}_2 = 1:1$ , rate of flow 400 cc/minute) in the presence  
of 1.45%  $\text{O}_3$  becomes apparent at the same temperature ( $100-110^\circ$ ) that  
decomposition of  $\text{O}_3$  begins. On this basis the authors consider that  
initiator action is associated not with the  $\text{O}_3$  molecule but with O  
atoms which are decomposition products of  $\text{O}_3$ .

1/1





KARMILOVA, L.V.; YENIKOLOPYAN, N.S.; NALBANDYAN, A.B.

Kinetic study of the initial phase of nitrogen oxide  
catalyzed oxidation of methane (with English summary in  
insert). Zhur.fiz.khim. 30 no.4:798-810 Apr. '56. (MLRA 9:9)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki, Moskva.  
(Methane) (Oxidation)

ANTONOVA, I. N., MOSHKINA, R. I., HALBANDYAN, A. B., NEYMAN, M. B., FEKLISOV, G. I.

"Tracer Study of the Mechanism of the Reaction of Methane Oxidation,"

Problemy Kintics and Catalysis, v. 9, Isotopes in Catalysis, Moscow, Izd-vo AN SSSR, 1957, 442p.

Most of the papers in this collection were presented at the Conference on Isotopes in Catalysis which took place in Moscow, Mar 31- Apr 5, 1956.

HALBANDYAN, A. B., HEYMAN, M. B., and EMANUEL, N. H.

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

NALBANDYAN A.B.

ANISONYAN, A.A.; GUDKOV, S.F.; YENIKOLOPYAN, N.S.; KLEYMENOV, N.A.;  
MARKEVICH, A.M.; NALBANDYAN, A.B.; SIDOROV, A.P.

Obtaining formaldehyde by direct oxidation of natural gas using  
atmospheric oxygen. Gaz.prom. no.6:32-40 Je '57. (MLRA 10:7)  
(Formaldehyde) (Gas, Natural) (Oxidation)

*NALBANDYAN, A.B.*  
MOSHKINA, R.I.; NALBANDYAN, A.B.; NEYMAN, M.B.; FEKLISOV, G.I.

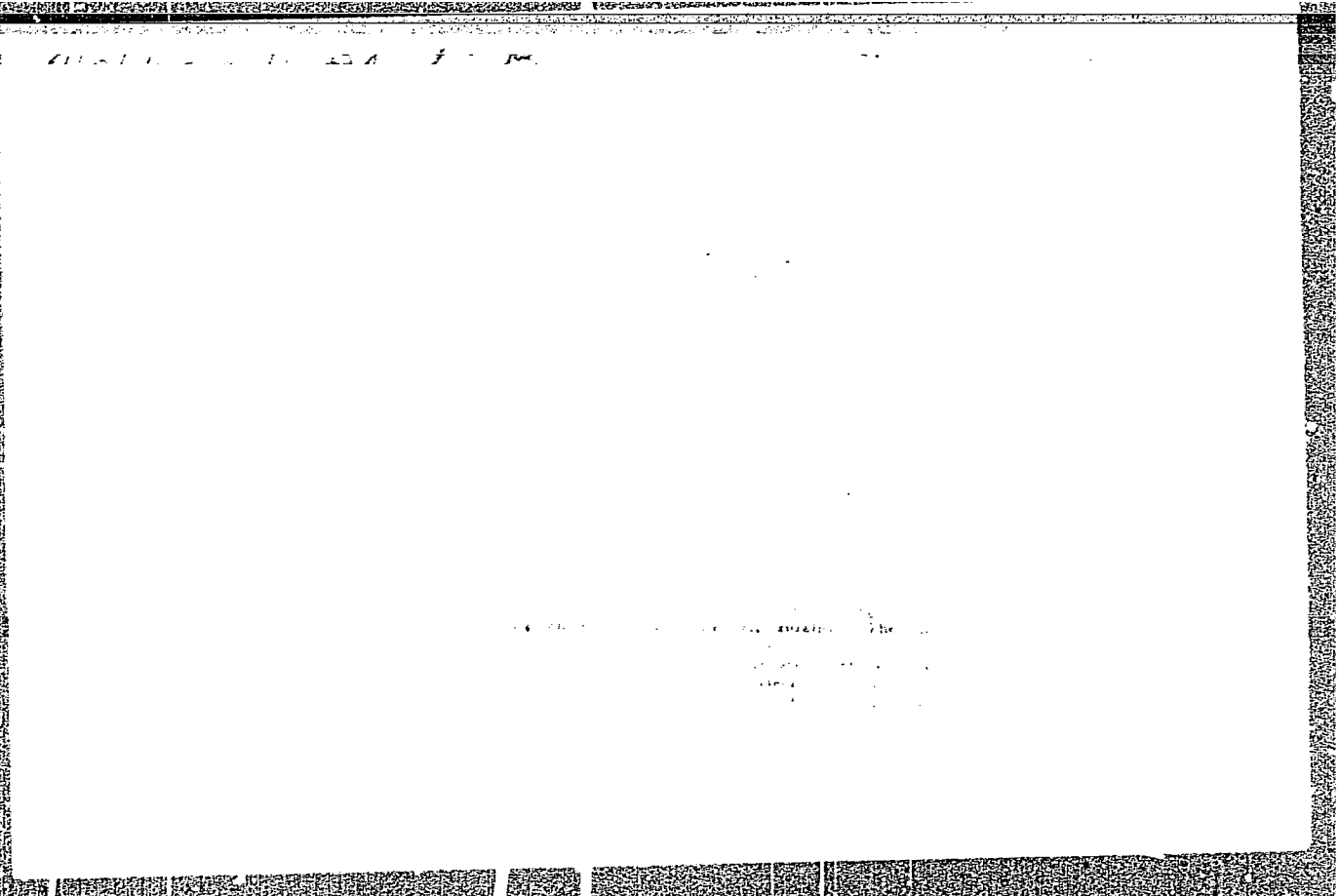
Tracer method for studying methane oxidation reaction. Report No.2:  
Mechanism of carbon dioxide formation. Izv.AN SSSR.Otd.khim.nauk.  
no.7:801-805 J1 '57. (MIRA 10:10)

1.Institut khimicheskoy fiziki AN SSSR.  
(Chemical reaction--Mechanism)  
(Carbon dioxide)

*NALBANDYAN, A.B.*

ANTONOVA, I.N.; MOSHKINA, R.I.; NALBANDYAN, A.B.; NEYMAN, M.B.; PEKLISOV, G.I.

Study of the mechanism of oxidation of methane using tagged atoms.  
Probl. kin. i kat. 9:97-103 '57. (MIRA 11:3)  
(Methane) (Oxidation) (Carbon--Isotopes)



ANISONYAN, A.A.; GUDKOV, S.F.; IVANOV, A.K.; YENIKOLOPYAN, N.S.;  
MARKEVICH, A.M.; NALBANDYAN, A.B.

Results of the operation of an experimental apparatus for  
the manufacture of formalin from natural gas. Trudy VNIIGAZ  
no.3:130-142 '58. (MIRA 11:8)  
(Natural gas) (Formaldehyde)



SOV/ 76-32-6-1/46

AUTHORS: Karmilova, L. V., Halbandyan, A. B.,  Semenov, N. N.

TITLE: An Investigation of the Combustion of Hydrogen with Oxygen Above the Lower Self-Ignition Limit (Issledovaniye kinetiki goreniya vodoroda s kislorodom nad nizhnim predelom samovzaplameneniya)

PERIODICAL: Zhurnal fizicheskoy khimii, 1958, Vol. 32, No. 6, pp. 1193-1204 (USSR)

ABSTRACT: The process of low-temperature self-ignition and the kinetics of combustion can be classified in 5 stages of reaction, the summary velocity of the combustion of hydrogen being determined by the modification of the concentration of atomic hydrogen. For this process a differential equation by N. N. Semenov exists. As may be seen from a diagram, the relative concentration of atomic hydrogen reaches comparatively high values during reaction, thus disturbing the relation between the pressure drop  $\Delta p$  and the consumption of substance. It was observed that the pressure drop is proportional to the combustion at low relative concentrations of atomic hydrogen.

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SOV/76-32-6-1/46

An Investigation of the Combustion of Hydrogen With Oxygen Above the Lower Self-Ignition Limit

A. A. Koval'skiy (Ref 2) found that the "chain ignition" is transformed into a "thermal ignition" at a higher initial pressure. In the present investigation measurements were conducted within a wide range of temperature and of pressure in order to determine the mechanism of combustion, the decomposition constant  $k_2$  and the activation energy  $E_2$  of the reaction  $H + O_2 \rightarrow OH + O$ . Data from publications available at present give different values for  $E_2$  as may be seen from papers by Warren (Ref 3), Koval'skiy (Ref 2), N. N. Demenov (Refs 4, 5), Lewis and Elbe (Ref 6) and V. V. Voevodskiy (Ref 7). It proceeds from the experimental part that the investigations were carried out at 460-600°, individual kinetic curves being given in this connection. The obtained results of the measurements accurately coincided with the theoretical curve of the combustion maxima, the constant of reaction velocity having, with one exception, practically identical values at all pressures. The value of the constant of reaction velocity  $k_2$  of the decomposition reaction five times exceeded that obtained in the papers by A. B. Nalbandyan and V. V. Voevodskiy. The value obtained by Baldwin, Corney and Simmons (Ref 12) is about the same. The activation energy

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SOV/76-32-6-1/46

An Investigation of the Combustion of Hydrogen with Oxygen Above the Lower Self-Ignition Limit

$E_2$  of the decomposition reaction was determined according to three different methods, all yielding identical results. Summarily, it can be stated on the strength of the evidence found that the maximum of reaction velocity is shifted to the range of low combustion with a reduction of  $R = 2p_1/p_0$ . This can be explained with the above mentioned phenomenon of the increase of concentration of hydrogen atoms. There are 12 figures, 4 tables, and 13 references, 9 of which are Soviet.

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

SUBMITTED: December 30, 1957

1. Hydrogen--Combustion
2. Combustion--Velocity
3. Oxygen--Chemical reactions
4. Mathematics

Card 3/3

*NAL BANDYAN, A. B.*

AUTHORS: Kleymenov, N. A., Nalbandyan, A. B. 20-1-35/58

TITLE: The Interaction Between Ozone and Methyl Hydroperoxide  
(O vzaimodeystvii mezhd u ozonom i gidroperekis'yu metila).

PERIODICAL: Doklady AN SSSR 1958, Vol. 118, Nr 1, pp. 125-127 (USSR)

ABSTRACT: Into an evacuated retort of a content of 8,5 l (which was kept at a given temperature in a thermostat) given quantities of hydroperoxide and then of ozonized oxygen were quickly introduced. The concentration of ozone exceeded in all experiments the concentration of peroxide 5-6fold. By means of the process discussed here peroxide can qualitatively be separated from ozone. The results of these experiments are given in a diagram which shows the dependence of the concentrations of methyl peroxide on the duration of keeping the reacting mixture at the temperatures of 25, 34, 43, 52 and 64°. The points are situated well on the corresponding curves within the frame of possible errors. From the kinetic curves the constants of the reaction velocity and from the temperature dependence of the constant K of the reaction velocity the activation energy of the interaction between ozone and methyl hydroperoxide were then determined. In the diagram for the dependence of the magnitude  $\lg K$  on  $1/T$  the experimental points

Card 1/3

## The Interaction Between Ozone and Methyl Hydroperoxide.

20.1-35/58

fit well on a straight line. From the tangent of the angle of inclination of this curve the value  $E = 7000$  kal/mol. was obtained for the activation energy. From the series of kinetic curves the following can be seen: if about 15 minutes are necessary for the decrease of the concentration of the peroxide by 50 % at  $25^{\circ}$  this time reduces to 2,5 minutes at  $64^{\circ}$ . With a reaction period of 25 minutes practically all the peroxide has decomposed under the influence of ozone. Besides these experiments a special investigation for the determination of the main products of reaction of the interaction between ozone and methyl hydroperoxide was made. The analysis of these products showed that peroxide under the influence of ozone transforms mainly into methyl alcohol. In the reaction products about 80% of methylated alcohol and about 6 % of formaldehyde were found. The primary products of the oxidation of the hydrocarbons in the presence of slowly decomposing ozone are the hydroperoxides of the corresponding hydrocarbons. The authors, however, could not determine them as, under the influence of not-decomposed ozone, they transformed completely into alcohols. There are 3 figures, 1 table, and 5 references, 2 of which are Slavic.

Card 2/3

The Interaction Between Ozone and Methyl Hydroperoxide.

20-1-35/58

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

PRESENTED: July 6, 1957, by V. N. Kondrat'yev, Academician.

SUBMITTED: June 26, 1957

AVAILABLE: Library of Congress

Card 3/3

SOV/20-122-1-28/44

5(4)

AUTHORS:

Kleymenov, N. A., Malbandyan, A. B.

TITLE:

Concerning the Problem of the Rôle of Ozone in the Initiation of the Reactions of Oxidation of Saturated Gaseous Hydrocarbons (K voprosu o roli ozona v initsirovanii reaktsiy okisleniya nasyshchennykh gazoobraznykh uglevodorodov)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 1, pp 103-105 (USSR)

ABSTRACT:

This paper gives some new data concerning the oxidation of propane and hydrogen which according to the authors' opinion confirm the mechanism of the action of ozone through the oxygen atoms. The experiments were carried out at atmospheric pressure. The products of the oxidation of propane - peroxides and aldehydes - were collected and then they were analyzed by the usual methods. The experimental data concerning the oxidation of hydrogen by ozonized oxygen are represented by a diagram. A noticeable decomposition of the ozone begins at a temperature of 85°, and also the oxidation of hydrogen begins at the same temperature. If the contact time increases from 21 to 40 sec, the temperature of the

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Concerning the Problem of the Rôle of Ozone in the Initiation of the Reactions of Oxidation of Saturated Gaseous Hydrocarbons

beginning of the decomposition of ozone (and also of the oxidation of hydrogen) is diminished to 20 - 25°. Similar results are found for the oxidation of propane. Also in this case, the beginning of the oxidation agrees with the decomposition of ozone. This coincidence apparently is caused by the formation of active particles - by atoms or by excited molecules of oxygen which initiate the chain reaction. By further experiments, the nature of the initiation was investigated. According to these results, the excited oxygen molecules do not play an essential rôle in the oxidation reaction and, therefore, the initiation of the reaction must be connected with a reaction of atomic oxygen. In order to investigate the correctness of this conclusion, the authors carried out experiments concerning the initiation of the reaction by oxygen atoms which were produced immediately in a mixture of methane and oxygen. The photochemical initiation was used for this purpose. If the methane-oxygen mixture (75 % CH<sub>4</sub> and 25 % O<sub>2</sub>) circulates under a pressure of 15 torr, ~ 9 % of the initial methane was oxidized to hydrogen peroxide, and ~ 7 % - to formaldehyde. This experiment took

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Concerning the Problem of the Rôle of Ozone in the Initiation of the Reactions of Oxidation of Saturated Gaseous Hydrocarbons

5 hours and the products of the reaction were frozen out at the temperature of the liquid nitrogen. It is very probable that formaldehyde is a secondary product of the photochemical decomposition of hydrogen peroxide. The following conclusion may be drawn from the data published in this paper and also in a previous paper: The oxidation of saturated gaseous hydrocarbons by ozonized oxygen is initiated by oxygen atoms produced by the thermal decomposition of ozone. There are 3 figures and 7 references, 1 of which is Soviet.

PRESENTED: April 24, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: April 17, 1958

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5(4)

SOV/20-122-3-27/57

AUTHORS:

Kleymenov, N. A., Nalbandyan, A. B.

TITLE:

The Investigation of the Reaction of the Low-Temperature Oxidation of Methane Initiated by Atoms of Oxygen Produced by the Thermal Decomposition of Ozone (Issledovaniye reaktsii nizektemperaturnogo okisleniya metana, initsirovannoy atomami kisloroda, obrazuyushchimsya pri termicheskom raspade ozona)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 3, pp 420-423 (USSR)

ABSTRACT:

According to the results of previous papers, the oxygen atoms produced by thermal decomposition of ozone initiate the oxidation of methane by ozonized oxygen. Under such conditions, methyl hydroperoxide and formaldehyde are the most important products of the reaction. It was necessary to investigate the dependence of the yield of these products on various parameters (composition of the mixture, concentration of ozone, time of contact etc.) and to compare the found relations with the results of the oxidation of methane and its higher homologues sensitized by mercury. The oxidation by ozonized oxygen was carried out at atmospheric pressure. A diagram shows the

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The Investigation of the Reaction of the Low-Temperature Oxidation of Methane Initiated by Atoms of Oxygen Produced by the Thermal Decomposition of Ozone

kinetic curves of the formation of methyl hydroperoxide, found at  $T = 150^{\circ}$  for 3 compositions of the mixture. The experiments were carried out for a constant concentration of ozone in the initial mixture. In the investigated time intervals, the yield of peroxide grows according to a linear law. A second diagram shows the relation between the yield of peroxide and formaldehyde as a function of the ozone concentration for an equimolecular mixture of methane and oxygen (contact time 21 sec, temperatures 150 and  $180^{\circ}$ ). The quantities of the produced peroxide and formaldehyde are proportional to the initial ozone concentration in the mixture. This linear relation applies as long as the waste gases (otkhodyashchiye gazy) contain ozone. In order to investigate the influence of methane upon the yield of methyl hydroperoxide, a special series of experiments was carried out at  $T = 150^{\circ}$ . According to the results found, the quantity of the produced peroxide grows linearly with the concentration. The amount of the decomposed ozone remains constant. Similar results were found for  $T = 180^{\circ}$ . If the concentration of oxygen during the experiments does not remain constant and if the oxygen contained

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SOV/20-122-3-27/57

- The Investigation of the Reaction of the Low-Temperature Oxidation of Methane Initiated by Atoms of Oxygen Produced by the Thermal Decomposition of Ozone

in the mixture is replaced by methane, the above-mentioned linear relation becomes a non-linear one. Other diagrams show the increase of the quantity of the decomposed ozone with the concentration of methane and the dependence of the peroxide yield on oxygen. For oxygen concentrations from 30 to 90 %, the quantity of the peroxide produced does not depend on the concentration of oxygen. According to a comparison of the results of this paper with the results of the photochemical oxidation of methane, ethane, and propane, the mechanism of oxidation is equal for both of these cases. There are 4 figures and 7 references, 6 of which are Soviet.

PRESENTED: May 23, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: May 21, 1958

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5(3)

PHASE I BOOK EXPLOITATION

SOV/3198

Nalbandyan, Aram Bagratovich, and Nikolay Sargseyevich Yenikolopyan

Formal'degid - material dlya plastmass (Formaldehyde: Raw Material for Plastics) Moscow, AN SSSR, 1959. 68 p. (Series: Akademiya nauk SSSR. Nauchno-populyarnaya seriya) 17,000 copies printed.

Resp. Ed.: V.N. Kondrat'yev, Academician; Ed. of Publishing House: V.N. Vyazentshev; Tech. Ed.: A.P. Guseva.

Sponsoring Agency: Akademiya nauk SSSR. Redkollegiya nauchno-populyarnoy literatury.

**PURPOSE:** This book is intended for chemists interested in plastics production, students of organic chemistry, and persons interested in the theory and practice of synthetic materials production.

**COVERAGE:** The booklet describes the nature of formaldehyde, its principal properties, methods for its production, and its most important chemical reactions with other substances to produce synthetic resins and plastics.

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Raw Material (Cont.)

SOV/3198

Also, some properties of formaldehyde products, and their industrial and domestic uses are reviewed. No personalities are mentioned. There are 10 Soviet references.

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Ch. I. Formaldehyde and Its Properties	5
Ch. II. The Production of Formaldehyde	9
Ch. III. Some Formaldehyde Polymers	19
Ch. IV. Phenol-formaldehyde Resins	31
Ch. V. Urea-formaldehyde and Some Other Resins	50
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AVAILABLE: Library of Congress

Card 2/2

TM/jb  
2-24-60

SOV/80-32-4-3B/47

The Preparation of Formaldehyde in a Jet Apparatus by Means of the Oxidation of Methane Catalyzed by Nitrogen Oxides

a vessel, in which reactions take place, with  $K_2B_4O_7$  increases and stabilizes the yield of formaldehyde and reduces the reaction temperature by 80 or 100°C; 2. The relative yield of formaldehyde ( $CH_2O : NO$ ) amounts to 10 to 12 molecules per one molecule of the catalyst; 3. The optimum composition of the methane-air mixture was found to be 1 : 2; 4. The optimum temperature of the reaction is about 100°C; 5. The stable run of the reaction is possible in metal vessels; 6. The laboratory results were confirmed by experiments carried out in a pilot installation with a capacity of 13 m<sup>3</sup>/hr of gas-air mixture. There are 7 graphs and 35 references, 16 of which are Soviet, 14 English, 2 German, 1 Swiss, 1 French and 1 Japanese.

SUBMITTED: September 30, 1957

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5 (4), 5 (3)  
AUTHORS:

Poroykova, A. I., Voevodskiy, V. V., SOV/76-33-6-26/44  
Nalbandyan, A. B.

TITLE:

Photoinitiation of Propane Oxidation in the Presence of  
Ammonia and Hydrogen Sulphide (Fotoinitsirovaniya oksileniya  
propana v prisutstvii ammiaka i serovodoroda)

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 6,  
pp 1336-1344 (USSR)

ABSTRACT:

The thermal oxidation of low, gaseous paraffin hydrocarbons proceeds only at high temperatures at a noticeable rate; the high temperature leads to a decay of the intermediate products so that these products as well as the reaction kinetics cannot be investigated under these conditions. A photochemical reaction initiation (RI) is, besides the catalysis, an important method of (RI). The photochemical oxidation of low gaseous hydrocarbons was first investigated by A. B. Nalbandyan et al (Refs 1-3), and among other things, a reaction mechanism of the propane oxidation at low temperature was suggested (i) - (8). The photolyses (P) of the ammonia (I) and hydrogen sulphide (II) have been insufficiently examined up to now; on the other hand, it

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## Photoinitiation of Propane Oxidation in the Presence of Ammonia and Hydrogen Sulphide SOV/76-33-6-26/44

must be assumed that at a (P) of (I) or (II) in the presence of a mixture of propane (III) and oxygen (IV), the resulting inorganic radicals will form propyl radicals with the molecules of (III), thus initiating the (III)-oxidation. The latter has already been observed (Refs 16, 17), the mode of origin of the formed acetone could not be clarified. The present experiments were carried out in a vacuum device (Fig 1), which was equipped with 2 quartz lamps PRK-2. The reaction products were frozen out by liquid nitrogen. The experiments led to the following statements: Isopropylhydroperoxide (V), acetaldehyde and formaldehyde form at 200-220°C as main products of the photochemical propane oxidation. The (RI) with (I) gives at 220°C a yield of reaction products of  $\gamma \geq 5$  per decomposed (I)-molecule, which is considered as a confirmation of the chain mechanism in the process. The present results as well as those obtained by A. B. Nalbandyan et al permit the assumption that the propane oxidation, photoinitiated with mercury (Refs 1-3), ammonia or hydrogen sulphide, proceeds according to the same chain mechanism, independent of the type of initiator. The acetone which - as

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Photoinitiation of Propane Oxidation in the Presence of Ammonia and Hydrogen Sulphide SOV/76-33-6-26/44

mentioned above - is observed in static experiments, is produced by the decay of (V). There are 5 figures, 1 table, and 23 references, 7 of which are Soviet.

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

SUBMITTED: November 27, 1957

Card 3/3

5 (4)

AUTHORS:

Anisonyan, A. A., Beyder, S. Ya., SOV/76-33-8-4/39  
Markevich, A. M., Nalbandyan, A. B. (Moscow)

TITLE:

A Study of the Oxidation and Decomposition Reactions of  
Formaldehyde at High Temperatures

PERIODICAL:

Zhurnal fizicheskoy khimii, 1959, Vol 33, Nr 8, pp 1695-1700 (USSR)

ABSTRACT:

In order to develop the technology of a methane oxidation to formaldehyde (I) it was necessary to study the stability of (I) in the reaction gas (Refs 1-2). Since the corresponding data found in publications refer to relatively low temperatures and longer contact times, and thus did not suffice for the desired purposes, special experiments were carried out in the present case. The oxidation and decomposition reactions of (I) were studied within the temperature range of 500-850° at a contact time of 0.3 seconds and atmospheric pressure. The studies were carried out in a flow unit (Fig 1). The (I) concentration in the initial gas mixtures was 1 % by volume throughout. The oxidation reaction was studied with a mixture air: (I) = 99 : 1 in an empty reaction vessel as well as in one filled with packing. It was found that the oxidation rate largely depends on the surface properties of the walls of the reaction vessel as well as on the S/V value. Washing

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A Study of the Oxidation and Decomposition Reactions of Formaldehyde at High Temperatures SOV/76-33-8-4/39

out the reaction vessel with a 2 %  $K_2B_4O_7$ -solution, and filling it with packings, resulted in a considerable retardation of the oxidation reaction of (I). NO additions (0.1 %) to the initial gas mixture greatly accelerates the reaction in the presence of oxygen. The decomposition reaction of (I) was studied in mixtures  $CH_4$  : (I) = 99 : 1 in the absence of oxygen, and it was found that there is no dependence of the decomposition rate (DR) upon the properties of the surface of the reaction vessel wall, or the S/V value. NO additions (up to 0.8 %) did not show any marked effect upon the (DR) either. There are 7 figures and 6 references, 4 of which are Soviet.

SUBMITTED: August 1, 1957

Card 2/2

5(4)

AUTHORS:

Kleymenov, N. A., Nalbandyan, A. B.

SOV/20-124-1-33/69

TITLE:

On the Ways of Forming Methyl-Hydroperoxide and Formaldehyde in the Reaction of Low Temperature Oxidation of Methane  
(O putyakh obrazovaniya gidroperekisi metila i formal'degida v reaktsii nizkotemperaturnogo okisleniya metana)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 124, Nr 1, pp 119-122 (USSR)

ABSTRACT:

On the basis of the oxidation of methane, this paper for the first time provides qualitative proof of the existence of parallel reactions leading to the formation of aldehydes and peroxides. Besides, the production rates of all these substances are determined. This problem was solved by employing the method of marked atoms. The reaction, which occurs at low temperatures, was photochemically initiated. The light source used was a mercury-quartz lamp PRK-2. For the purpose of a maximum utilization of energy, a quartz device of special construction was developed, which makes irradiation from the interior of the reactor possible. By means of provisional tests carried out at 360°, it was found that, within the interval of time under investigation, no other products besides peroxide

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On the Ways of Forming Methyl-Hydroperoxide and SOV/20-124-1-33/69  
Formaldehyde in the Reaction of Low Temperature Oxidation of Methane

and formaldehyde were formed. In order to intercept these substances, gases emerging from the reactor were allowed to pass through aqueous absorbers. The concentration of the peroxide in the solution was idiometrically determined. The authors also developed a new method of determining formaldehyde. A diagram shows the kinetic curves of the production of  $\text{CH}_3\text{OOH}$  and  $\text{CH}_2\text{O}$  at  $360^\circ$ . The yield in connection with these products is, within the interval of time under investigation, a linear function of the duration of the contact. The second diagram shows the variation of the specific activities of peroxide and formaldehydes. The existence of an activity in the formaldehyde shows that a certain portion of the peroxide decays or is oxidized into formaldehyde. It is characteristic of the result obtained by the present paper that the curve for the specific activity of peroxide in its entire extent develops above the curve for the specific activity of formaldehyde. Such a behavior of specific activity is known to be characteristic of parallel reactions. At the temperature used in the present case about 64% of the methane participating in the reaction go over

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On the Ways of Forming Methyl-Hydroperoxide and SOV/20-124-1-33/69  
Formaldehyde in the Reaction of Low Temperature Oxidation of Methane

into formaldehyde by the immediate decay of the peroxide radical. Only 36% of the methane is transformed into hydroperoxide by the reaction with the peroxide radical. The ratio of the production rates of formaldehyde and peroxide is  $W_f/W_p = 1.75$ , and herefrom it is possible to determine the difference  $\Delta E$  between the activation energies of the isomerization and decay processes of the peroxide radical and its reaction with methane. The authors found  $\Delta E \approx 9600$  cal/mol. There are 2 figures, 1 table, and 10 references, 9 of which are Soviet.

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

PRESENTED: July 28, 1958, by V. N. Kondrat'yev, Academician

SUBMITTED: July 24, 1958

Card 3/3

5.3200  
5.4300

69136

## AUTHORS:

Karmilova, L. V., Yanikolopyan, N. S.,  
Nalbandyan, A. B. (Moscow)S/076/60/034/03/009/038  
B115/B016

## TITLE:

Kinetics and Mechanism of Methane Oxidation. I. Fundamental  
Macrokinetic Rules

## PERIODICAL:

Zhurnal fizicheskoy khimii, 1960, Vol 34, Nr 3, pp 550 - 558  
(USSR)

TEXT: The papers by N. N. Semenov (Refs 1,2) dealing with the oxidation processes of hydrocarbons are mentioned. In the present paper the results of a thorough investigation of the kinetics and composition of the oxidation products of methane during the entire course of reaction in a vessel with exactly prescribed type of surface are given. The rules in the accumulation of intermediates ( $\text{CH}_2\text{O}$  and  $\text{H}_2\text{O}_2$ ), some new phenomena in methane oxidation, and the probable mechanism of the process will be dealt with in the following publications of this series. The experiments were carried out in a static device already previously described (Ref 4). To analyze the formaldehyde and hydrogen peroxide a calorimeter of the type FEK-M was used. The experiments were made in a temperature range of from 423 to 513°C, in a pressure range of from 117 to 375 torr, and at ratios of  $\text{CH}_4:\text{O}_2 = 0.5; 1$  and 2 (Figs 1-3), in which connection the

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Kinetics and Mechanism of Methane Oxidation.  
I. Fundamental Macrokinetic Rules

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B115/B016

accumulation of reaction products ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ ,  $\text{H}_2\text{O}$ ) was pursued. The reaction kinetics in dependence on temperature (Fig 4), and the influence exercised by the composition of the initial mixture and initial pressure upon the kinetics of methane oxidation (Figs 5,6) were pursued. It is pointed out that the maximum rates of the consumption of initial reagents and accumulation of end products of the reaction in the temperature range investigated are in agreement with the stoichiometric ratios. The activation energy of methane oxidation is  $41.5 \pm 1$  kcal/mole. The dependence of the maximum rate of methane consumption on the initial pressure of the reaction mixture and its logarithmic anamorphosis is pursued (Fig 7). The degree of the completeness of the reaction of methane oxidation ( $n = 2.7$ ), the reaction degree for methane ( $\alpha = 1.62$ ), and that for oxygen ( $\beta = 0.96$ ) at a total pressure of  $\gamma \approx 0.1$ , were determined (Figs 8,9). The dependence of the induction period on the pressure of the initial mixture and its logarithmic anamorphosis are given (Fig 10). The temperature coefficient ( $E_{\tau_i} = 36 \pm 1$  kcal/mole) was also determined. The student V. T. Il'in also assisted in this investigation. There are 10 figures and 22 references, 10 of which are Soviet.

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Kinetics and Mechanism of Methane Oxidation.  
I. Fundamental Macrokinetic Rules

8/076/60/034/03/009/038  
B115/B016

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

SUBMITTED: June 5, 1958

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S/076/60/034/05/08/038  
B010/B0025.3400 (B)  
5.3200  
AUTHORS: Karmilova, L. V., Yenkolopyan, N. S., Nalbandyan, A. B.

TITLE: Kinetics and Mechanism of Methane Oxidation. II. Kinetics of Accumulation of Intermediates //

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 5, pp. 990-994

TEXT: The investigation under review was conducted with the participation of I. Yu. Uvarova. The authors studied the kinetics of accumulation of formaldehyde and hydrogen peroxide in the methane oxidation in a quartz vessel treated with HF. The influence of temperature was tested with a stoichiometric methane - oxygen mixture at 235 torr pressure and temperatures of 426, 472, 491.5, and 513°C (Figs. 1-4, kinetic curves). The analysis of the curves showed that formaldehyde appears as primary intermediate, while hydrogen peroxide is formed after longer contact times by oxidation of formaldehyde. The maximum concentration of formaldehyde rises with temperature, while that of hydrogen peroxide drops. The yield of hydrogen peroxide drops likewise with a rise in temperature. The activation energy of the formaldehyde formation amounts to  $E(\text{CH}_2\text{O})_{\text{max}} = 7.8 \pm 0.5 \text{ kcal.}$

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Kinetics and Mechanism of Methane Oxidation.  
II. Kinetics of Accumulation of  
Intermediates

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B010/B002

The maximum yield of formaldehyde increases in proportion to a rise in the initial pressure of the gas mixture. While the yield of hydrogen peroxide depends but little on the formaldehyde content in the mixture, the maximum yield of formaldehyde rises linearly with rising methane content in the gas mixture. With ratios  $O_2 : CH_4 = 2$  to  $0.86$ , the maximum yield of formaldehyde is independent of the oxygen content in the gas mixture, whereas in the case of  $O_2 : CH_4 = 0.86$  to  $0.128$ ,  $CH_2O_{max}$  drops linearly with dropping oxygen partial pressure. A paper by A. M. Markevich is mentioned in the text. There are 11 figures and 13 references: 8 Soviet and 5 English.

SUBMITTED: June 5, 1958

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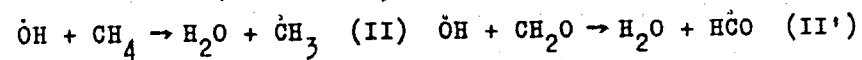
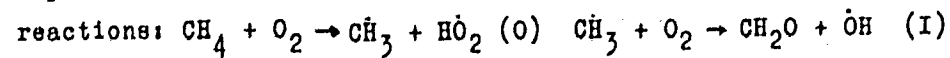
81565  
S/076/60/034/06/04/040  
B015/B061

AUTHORS: Karmilova, L. V., Yenikolopyan, N. S., Nalbandyan, A. B.,  
Semenov, N. N. (Moscow)

TITLE: Kinetics and Mechanism of the Oxidation of Methane.  
III. Detailed Mechanism of the Reaction

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 6,  
pp. 1176-1185

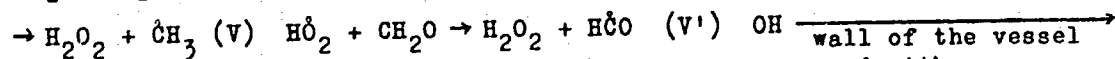
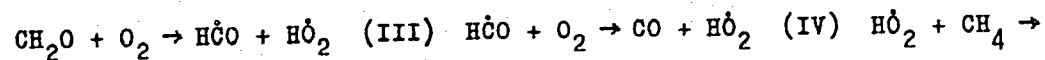
TEXT: On the basis of the kinetic data and the modern conception of the energy of elementary reactions of radicals with stable molecules, a scheme of the most probable oxidation mechanism of methane in the gaseous phase is derived, with due consideration of the branch reaction of formaldehyde in the process. The oxidation mechanism can be represented to greater degrees of conversion by the following system of



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Kinetics and Mechanism of the Oxidation of  
Methane. III. Detailed Mechanism of the  
Reaction

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B015/B061



Calculated data of the maximum rate of oxidation compared with experimental data are given in Table 1 for temperatures of 472°, 491.5° and 513°C, and the values of the kinetic parameters of the methane oxidation in Table 2. The quantitative agreement of the values calculated according to the derived mechanism with those of the experimental data confirm the validity of the proposed reaction mechanism.

L. I. Avramenko, A. M. Markevich, and V. V. Voyevodskiy are mentioned in the text. There are 2 tables and 20 references: 14 Soviet, 4 British, and 1 Canadian.

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

SUBMITTED: June 23, 1958

Card 2/

S/020/60/132/04/36/064  
B004/B007

AUTHORS: Azatyán, V. V., Voyevodskiy, V. V., Corresponding Member of  
the AS USSR, Nalbandyan, A. B.

TITLE: Determination of the Rate Constant of the Reaction of Atomic  
Oxygen With Molecular Hydrogen ||

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 4, pp. 864-867

TEXT: For the reaction  $O + H_2 = OH + H$  (III) the rate constant  $k_{III}$  was determined by measuring the lower flash point of  $CO + O_2$  mixtures in the case of various additions of  $H_2$ . On the basis of the reaction mechanism suggested in publications, among them those by V. N. Kondrat'yev (Ref. 6), N. S. Yenikolopyan and A. B. Nalbandyan (Ref. 7), the authors derive equation (1) for the flash point and equation (3) for the dependence between the total pressure  $P$  and the partial pressures  $P_{O_2}$  and  $P_{H_2}$ , and finally equation (8) for  $\log(\tan \alpha / bT^{2.5})$ , where  $\tan \alpha$  and the factor  $b$

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Determination of the Rate Constant of the  
Reaction of Atomic Oxygen With Molecular  
Hydrogen

S/020/60/132/04/36/064  
B004/B007

are graphically to be determined. The experiments were carried out in a vacuum vessel. Fig. 1 shows the dependence of the flash point for mixtures of  $2CO + O_2 + xH_2$  at different temperatures, and Fig. 2 the dependence of  $P_{pO_2}$  on  $1/P_{pH_2}$ . Herefrom it was possible to determine  $\tan \alpha$  and  $b$  (Fig. 3). ✓

For the constant  $k_{III}$ ,  $k_{III} = 1.5 \cdot 10^{-10} \exp(-\frac{12,100+400}{RT}) \text{ cm}^3 \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$  was found. There are 3 figures and 11 references: 6 Soviet, 1 British, and 1 German.

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

SUBMITTED: February 9, 1960

Card 2/2



81406

S/020/60/132/06/31/068  
B004/B005

5.3200

AUTHORS: Gorban', N. I., Nalbandyan, A. B.

TITLE: Determination of Rate Constants for Elementary Reactions of Hydrogen Atoms With Hydrocarbons<sup>1</sup>

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 6, pp. 1335-1338

TEXT: The authors discuss the papers by N. N. Tikhomirova and V. V. Voevodskiy (Ref. 2) who found the constants of the reaction  $H + RH = H_2 + R$  (I) by determining the lowering of the upper ignition point in hydrogen-hydrocarbon mixtures. The authors suggest a variation of this method which facilitates a more accurate determination of the constants and the activation energy of the atomic hydrogen with various hydrocarbons, and is based on measuring the raising of the lower ignition point. This determination is made in the temperature range 400 - 550°C where the influence of water vapor and the reaction of  $HO_2$  with other molecules are still negligibly small. Equation (II) is written down:  $2K_2(O_2) = K_4 + K_5(RH)$ ; X

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Determination of Rate Constants for Elementary  
Reactions of Hydrogen Atoms With Hydrocarbons

S/020/60/132/06/31/068  
B004/B005

where  $K_2$  is the rate constant of the reaction  $H + O_2 = OH + O$ ,  $K_4$  the rate constant of the adsorption of H atoms by the walls of the reaction vessel, and  $K_5$  the rate of the reaction (I). Equation (IV) is derived:  $\Delta P/P_{RH} = 3/2(K_5/K_2)$ , where  $\Delta P$  is the difference of the partial pressures of oxygen at the lower ignition point in the presence of the inhibitor RH and without an inhibitor,  $P_{RH}$  is the partial pressure of the inhibiting hydrocarbon.  $K_5$  can be computed from the experimentally found  $\Delta P$  and  $P_{RH}$ , as well as the values for  $K_2$  indicated in Ref. 5. Equation (V) is obtained by introducing the energy equations  $K_5 = K_5^0 \exp(-E_5/RT)$  and  $K_2 = K_2^0 \exp(-E_2/RT)$ , and by taking the logarithm.  $\Delta E = E_2 - E_5$  is determined from the inclination of the straight line in the diagram  $\log(\Delta P/P_{RH})$ ,  $1/T$ . The lower ignition point of  $H_2 - O_2$  mixtures was determined in a quartz vessel which had been washed with hydrofluoric acid, distilled water, and 2% potassium

Card 2/3

81406

Determination of Rate Constants for Elementary Reactions of Hydrogen Atoms With Hydrocarbons S/020/60/132/06/31/068  
B004/B005

tetraborate. Low measurement values were obtained in this way. Inflammation was recorded by means of a diaphragm manometer. Figs 1, 2 show the temperature dependence of the lower ignition points for  $2\text{H}_2 + \text{O}_2$ , and with the addition of 0.6% of  $\text{C}_2\text{H}_6$  or 0.4% of  $\text{C}_3\text{H}_8$ . Table 1 indicates the values for  $K_5$  and  $E_5$  with the addition of ethane, propane, or butane, Figs. 3, 4 show the linear dependence of the  $\log(\Delta P/P_{RH})$  on  $1/T$  with the addition of ethane or propane. The values obtained are higher than those indicated in Ref. 1, and come near to those measured by E. W. R. Steacie (Ref. 11). There are 4 figures, 1 table, and 6 references: 4 Soviet, 6 British, and 1 American.

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

PRESENTED: February 5, 1960, by V. N. Kondrat'yev, Academician

SUBMITTED: February 2, 1960

Card 3/3

88242

S/195/60/001/003/001/013  
B002/B058

11.1000

AUTHORS: Ivanov, O. A., Nalbandyan, A. B.

TITLE: On the Dependence of the Lower Self-ignition Limit of Hydrogen-oxygen Mixtures on Their Composition

PERIODICAL: Kinetika i kataliz, 1960, Vol. 1, No. 3, pp. 337 - 339

TEXT: The lower self-ignition limit of hydrogen-oxygen mixtures was measured at 430°C (1), 470°C (2), and 520°C (3). A quartz vessel was used which was cleaned with concentrated hydrofluoric acid and then treated with a 2% solution of potassium tetraborate. The lower self-ignition limit was determined by measuring the pressure change. Fig. 1 shows the dependence of the limit pressure  $P_{lim}$  (mm Hg) on the mol fraction  $\gamma = [O_2 / (H_2 + O_2)]$ . X

The equation  $P_{lim} \cdot \gamma = \text{const}$  derived according to the theory by N. N. Semenov is strictly valid between 5 and 50%  $O_2$ . For the adhesion of the H atoms to the walls of the quartz vessel at  $\gamma < 0.5$ , the probability  $\xi_H$

Card 1/3

88242

On the Dependence of the Lower Self-ignition Limit of Hydrogen-oxygen Mixtures on Their Composition

S/195/60/001/003/001/013  
B002/B058

was calculated as  $4.38 \cdot 10^{-5}$ ,  $5.24 \cdot 10^{-5}$ , and  $6.36 \cdot 10^{-5}$ . The temperature dependence of  $\epsilon_H$  is given by formula:

X

$$\epsilon_H = \epsilon_0 \exp\left(\frac{-E_{\epsilon_H}}{RT}\right)$$

$E_{\epsilon_H}$  resulted as 4.6 Kcal/mole. A. Biron, L. V. Karmilova are mentioned. There are 2 figures and 4 Soviet references.

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

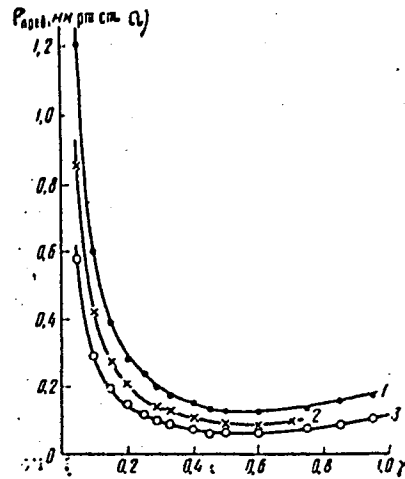
SUBMITTED: January 20, 1960

Card 2/3

88242

S/195/60/001/003/001/013  
B002/B058

Legend to Fig. 1: 1) 430°C; 2) 470°C;  
3) 520°C, a)  $P_{lim}$ , mm Hg



Card 3/3

R/003/60/011/007/002/003  
A125/AC26

AUTHORS: Kleimenov, N.A.; Nalbandyan, A.B.

TITLE: Oxidation of Methane at Low Temperatures ✓

PERIODICAL: Revista de Chimie, 1960, Vol. 11, No. 7, pp. 391 - 401

TEXT: Subject article deals with the oxidation of methane at low temperatures. Brief reference is made to the authors of several methods of methane oxidation, including the oxidizing reaction at low temperature (Refs. 3 and 4). Out of these methods, the authors selected the following two, which have been employed by the Laboratory of Hydrocarbon Oxidations at the Physico-Chemical Institute of the Soviet Academy of Sciences in Moscow, to explain the oxidation mechanism of hydrocarbons at low temperatures: I. Oxidation of hydrocarbons by photochemical sensitization with mercury, worked out by the authors (Refs. 5 - 7). J.A. Grey (Ref. 13) examined the oxidation of ethane and methane. The authors (Ref. 15) studied the oxidation of methane. They all came to the conclusion that the oxidation of hydrocarbons at low temperatures takes place according to a unitary mechanism by the corresponding alkyl and hydroperoxide radicals. II. Utilization of ozone as initiator in the oxidizing reaction. On the basis

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R/003/60/011/007/002/003  
A125/A026

Oxidation of Methane at Low Temperatures

of the results obtained by different authors (Refs. 17 - 28), it can be concluded that the formation of the reaction products is conditioned not only by the direct interaction of the hydrocarbon and ozone molecules, but also a catalytic action of the ozone is performed. Reference is made to the reaction mechanism recommended by Norrisch (Ref. 27). Pease and his co-workers (Refs. 29 - 31) came to the conclusion that the stable primary products of the oxidation of hydrocarbons are the corresponding alcohols. According to the authors (Refs. 32 and 33), in the oxidizing reaction of methane initiated by ozone, the initial oxidizing product is not alcohol but methyl hydroperoxide. In order to explain the discrepancy between these two results, the authors conducted several experiments. The study of the reaction of methyl hydroperoxide was carried out with a special vacuum installation (Fig. 1) at 25, 34, 43, 52 and 64°C. The analysis of the products proved that 80% of the initial peroxide passes over into CH<sub>3</sub>OH, and approximately 6% into CH<sub>2</sub>O. The kinetic oxidation of methane in the presence of small amounts of ozone was carried out by using the jet method in the installation shown in Figure 3. Experiments on the thermal decomposition of ozone proved that the oxidizing reaction of methane appears only at the beginning of the thermal decomposition of ozone and is produced not by ozone, but by its decomposition products. Another experiment proved that, indifferent from the com-

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Oxidation of Methane at Low Temperature

R/003/60/011/007/002/003  
A125/A026

position of the mixture, the beginning of the ozone decomposition remains constant. S.I. Pshezhetskiy and his co-workers (Ref. 37) reported the same fact in case of butane. On the basis of these results, the authors concluded (Refs. 32, 33, 38 and 39) that the oxidation reaction is initiated by oxygen atoms formed by the decomposition of ozone. A series of experiments was carried out to explain the dependence of methyl hydroperoxide (Fig. 10) and formaldehyde (Fig. 11) from the initial ozone concentration. After examining the influence of methane and oxygen on the efficiency of methyl hydroxide, the authors came to the conclusion that the oxidation reaction of hydrocarbons at low temperatures is initiated by oxygen formed in the thermal decomposition. For direct determination of oxygen atoms in the reaction zone the method of Gheidon (Ref. 43) was used. These experimental results prove that ozone is only the carrier of oxygen, which initiates the oxidation of methane. S.I. Pshezhetskiy (Ref. 44) came to the same conclusion. The oxidation of methane initiated by ozone confirms the general conclusion that the oxidation of hydrocarbons at low temperature has a chain character, the chain being supported by alkylic and peroxydic radicals. There are 16 figures and 44 references: 21 Soviet, 8 German, 12 English, 2 Swiss and 1 Un-identified. ✓

ASSOCIATION: Physical-Chemical Institute of the USSR Academy of Sciences in Moscow

Card 3/3

KARMILOVA, L.V.; YENIKOLOPYAN, N.S.; NALBANDYAN, A.B. (Moscow)

Kinetics and mechanism of methane oxidation. Part 1. Zhur. fiz.  
khim. 34 no.3:550-558 Mr '60. (MIRA 13:11)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki.  
(Methane) (Oxidation)

30918

S/195/61/002/003/003/009

E111/E130

11.6200(also 3619)

AUTHORS: Azatyan, V.V., Voyevodskiy, V.V., and Nalbandyan, A.B.

TITLE: Determination of the rate constant for the reaction of atomic oxygen with molecular hydrogen

PERIODICAL: Kinetika i kataliz, v.2, no.3, 1961, 340-349

TEXT: The reaction of atomic oxygen with molecular hydrogen to give the hydroxyl radical and atomic hydrogen often occurs in the oxidation process, sometimes playing an important part. This reaction has not been sufficiently studied and there are no reliable published data on its rate constant. The authors have used a new method for making this determination. The velocity constants were measured by observing the flame boundaries in the burning of carbon monoxide in the presence of varying small concentrations of hydrogen. A conventional type of reaction apparatus was used, but it was found that the quantities reacting could be increased by coating the walls of the reaction chamber. NaCl and KCl coatings gave a several-fold increase, but MgO gave an increase of about fifty times, and therefore all work was done with magnesia-coated chambers, since much sharper flame-edge

Card 1/ 4

Determination of the reaction velocity.. <sup>30918</sup>  
S/195/61/002/003/003/009  
E111/E130

resolution could be obtained. The reaction oven temperature was controlled to  $\pm 0.2$  °C. Fig.2 shows values of the ignition limits as functions of temperature (570-660 °C) for a mixture of  $2H_2 + O_2$  (curve 1) and mixtures of  $2CO + O_2$  with 5.26, 3.06 and 1.01%  $H_2$  (curves 2, 3 and 4 respectively) for the 55-mm diameter vessel; results for  $2CO + O_2$  mixtures with 7.95, 4.15, 2.04 and 0.695%  $H_2$  are shown by curves 1, 2, 3 and 4 respectively in Fig.6. The work showed that the main carriers in the chain are OH and O, that the main reaction in the recombination of O and H atoms is their destruction on the vessel walls, and that the heterogeneous chain-breaking occurs in the diffusion region. The reaction temperature was varied between 570 and 660 °C and the hydrogen content of the mixtures from 0.7% to 8%. Because of the sharp edge definition possible, the reaction occurred under conditions of:

$$ed/\lambda \gg 1,$$

where  $e$  is the effectiveness of recombination of active centers at the surface,  $d$  the diameter of the vessel, and  $\lambda$  the mean free path (as verified by addition of inert nitrogen gas).

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Determination of the reaction ...

30918  
S/195/61/002/003/003/009  
E111/E130

Confirmation of the correctness of the approach used was obtained by independent calculations using diffusion in coefficient values. The rate-constant values for the reaction  $O + H_2 = OH + H$  was found to be  $1.11 \times 10^{-10} e^{-11700/RT}$  and for  $H + O_2 = OH + O$ ,  $1.30 \times 10^{-10} e^{-15900/RT}$

$cm^3, molecule^{-1} \cdot sec^{-1}$ .

L.I. Abramenko, R.V. Lorentso, V.N. Kondratyev and N.S. Yenikolopyan are mentioned for their contributions in this field. There are 8 figures, 3 tables and 30 references: 13 Soviet-bloc, 1 Russian translation from non-Soviet publication, 1 English translation from a Soviet author, and 15 non-Soviet-bloc. ✓

The four most recent English language references read as follows:

Ref.20: D.R. Warren, Trans. Faraday Soc., v.53, 199, 1957.

Ref.21: D.R. Warren, Trans. Faraday Soc., v.53, 206, 1957.

Ref.22: I.G. Greaves, J.W. Linnet, Trans. Faraday Soc., v.54, 1323, 1958.

Ref.29: P. Gray, Trans. Faraday Soc., v.55, 408, 1959.

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30918

Determination of the reaction velocity..

S/195/61/002/003/003/009

E111/E130

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

SUBMITTED: February 21, 1961

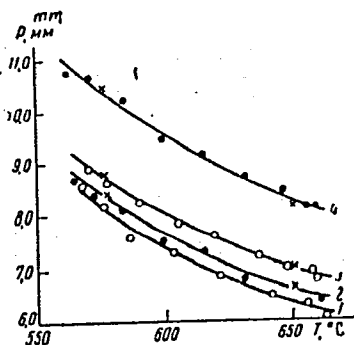


Fig. 2

Card 4/4

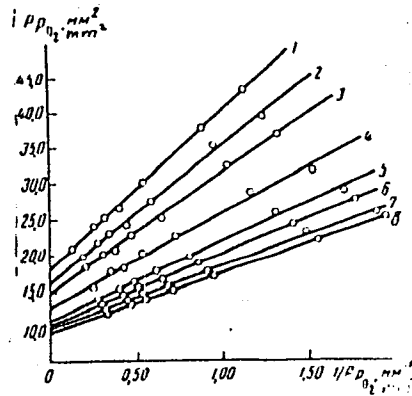


Fig. 6

AZATYAN, V.V.; AKOPYAN, L.A.; HALBANDYAN, A.B.

Electron paramagnetic resonance method used for detecting atomic hydrogen in a rarefied flame of a moist mixture of CO and O<sub>2</sub>. Kin.i kat. 2 no.6:940-941 N-D '61. (MIRA 14:12)

1. Institut khimicheskoy fiziki AN SSSR.  
(Hydrogen--Spectra) (Carbon monoxide)  
(Oxygen)

5.4300  
26.2510

27384  
S/171/61/014/003/001/004  
E071/E435

**AUTHORS:** Mantashyan, A.A., Moshkina, R.I. and Nalbandyan, A.B.

**TITLE:** On the behaviour of the methyl peroxide radical in the reaction of low temperature oxidation of methane

**PERIODICAL:** Akademiya nauk Armyanskoy SSR, Izvestiya. Khimicheskiye nauki. v.14, no.3, 1961, pp.185-195

**TEXT:** A study was made of the behaviour of the methyl peroxide radical within a wide range of temperatures in the reaction of oxidation of methane photosensitized with mercury, the difference between the activation energies of isomerization and decomposition of the peroxide radical and its reaction with methane was determined. The residence time of the reaction mixture in the irradiation zone was varied from 2 to 8-10 sec. The experiments were carried out at atmospheric pressure within the temperature range: room temperature to 400°C. A quartz lamp ПРК-2 (PRK-2) was used as a source of radiation, it was placed inside the reactor which consisted of three quartz tubes, placed co-axially. The lamp, placed in the internal tube, was cooled with circulating distilled water. The space between the first and second tube was  
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27384

S/171/61/014/003/001/004

On the behaviour of the methyl ... E071/E435

continuously evacuated with high vacuo pumps. The space between the second and the third tube served as a preheater and a reactor. Before passing into the reactor, the reaction mixture (90% CH<sub>4</sub>, 10% O<sub>2</sub>) was saturated with mercury vapour at room temperature. For the determination of the velocity of formation of methyl hydroperoxide and formaldehyde, methyl hydroperoxide marked with C<sup>14</sup> was introduced into the reaction mixture. The experimental procedure used was described previously (Ref.8: N.A.Kleymentov, Candidate dissertation. IKhF AN SSSR, 1959; Ref.9: R.I.Moshkina, N.L.Galanina, A.B.Nalbandyan, Izv. AN SSSR, OKhN 10, 1725 (1959)). It was found that the yield of oxidation products, calculated for 1 litre of the reaction mixture passed through the reactor, increases linearly with increasing residence time of the mixture in the irradiation zone (up to 10 sec). Within the range of temperatures studied, the yield of the peroxide increases with temperature, reaches a maximum (280 to 310°C) and then sharply decreases to zero. Formaldehyde appears in the reaction products later than peroxide and its yield is continuously increasing. On the basis of velocities of formation of formaldehyde (W<sub>a</sub>) and methyl hydroperoxide (W<sub>n</sub>), it was calculated that at 300°C about

X

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27384

S/171/61/014/003/001/004

On the behaviour of the methyl ... E071/E435

57% of methane, consumed in the reaction, is transformed into formaldehyde by-passing the methyl hydroperoxide stage. Of the total formaldehyde formed at a given temperature only 7% is formed from peroxide on its thermal decomposition. On the basis of the ratios of  $W_a/W_n$  (determined for the temperature range 190 to 325°C) the difference in the activation energies  $\Delta E$  of the processes of isomerization and decomposition of the peroxide radical and its reaction with methane was determined ( $\Delta E = 8500$  cal/mole). From the above data the ratio of the velocity constants of the reactions  $CH_3OO \rightarrow CH_2O + OH$  (4) and  $CH_3COO + CH_4 \rightarrow CH_3COOH + CH_3$  (2) was calculated:  $K_4/K_2 = 2.5 \times 10^{22} \text{ cm}^{-3}$ . There are 4 figures and 10 references: 9 Soviet and 1 non-Soviet. The reference to the English language publications reads as follows:  
H.Callender, Engineering 123, 147, 182, 210 (1927); A.C.Egerton, L.Smith, A.R.Ubbelohde, Phib. Trans. A.234, 433 (1953) E.W.Mardies, J.Chem. Soc. 1928, 872; J.A.Gray, J.Chem. Soc. 1952, 3150.

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

SUBMITTED: March 19, 1961  
Card 3/3

34620

S/171/61/014/006/001 001  
E075/E136

5,3300

**AUTHORS:** Mantashyan, A.A., and Nalbandyan, A.B.

**TITLE:** Photochemical oxidation of ethane sensitized with mercury vapour. Part I. Reaction at room temperature

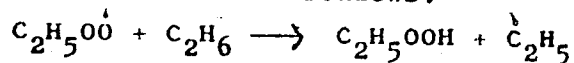
**PERIODICAL:** Akademiya nauk Armyanskoy SSR. Izvestiya. Khimicheskiye nauki, v. 14, no. 6, 1961. 517-526

**TEXT:** The authors investigated the kinetics and mechanism of photochemical oxidation of ethane at room temperature. The mixture of reactants was saturated with Hg vapour at 20 °C and was passed into an evacuated glass reactor. It was subjected to the action of light from a quartz-mercury lamp ПРК-2 (PRK 2) for a few seconds and was then removed from the reactor. Reactions at high temperatures were carried out by placing the reactor in an electrical furnace. It was established that the reaction products are ethylhydroperoxide and acetaldehyde forming in approximately equal quantities, independent of each other. It was found that the ratio of hydroperoxide/acetaldehyde depends on the surface/volume ratio of the reactor. Influence  
Card 1/3

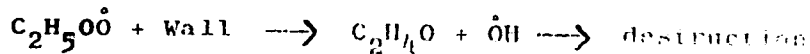
Photochemical oxidation of ethane ...

S/171/61/014/006/001/007  
E075/E136

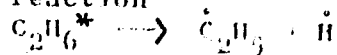
of the composition and pressure of the reacting mixture was investigated and it was concluded that ethylhydroperoxide forms in a bimolecular reaction as follows:



Acetaldehyde forms as a result of a heterogeneous destruction of the hydroperoxide radical on the walls of the reactor according to the following reaction:



The authors proposed a reaction mechanism in which excited Hg atom forming by absorption of light quantum of wavelength  $\lambda = 2537 \text{ \AA}$  transmits its excitation energy to hydrocarbon molecules on collision. The excited molecules decompose either according to the reaction



Card 2/3

Photochemical oxidation of ethane... S/171/61/014/006/001/001  
E075/E136

or are deactivated on collision with ethane molecules.  $C_2H_5^*$   
radical gives peroxide radical on collision with an  $O_2$   
molecule. The latter either forms a molecule of hydroperoxide  
or is destroyed at the reactor walls.  
There are 6 figures.

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

SUBMITTED: December 19, 1961

✓

Card 5/3

34621

S/171/61/014/006/002/005  
E075/E136

5.3300

**AUTHORS:** Mantashyan, A.A., and Nalbandyan, A.B.

**TITLE:** Photochemical oxidation of ethane sensitized with mercury vapour.  
Part II. Reaction at high temperatures.

**PERIODICAL:** Akademiya nauk Armyanskoy SSR. Izvestiya.  
Khimicheskiye nauki, v.14, no.6, 1961, 527-536

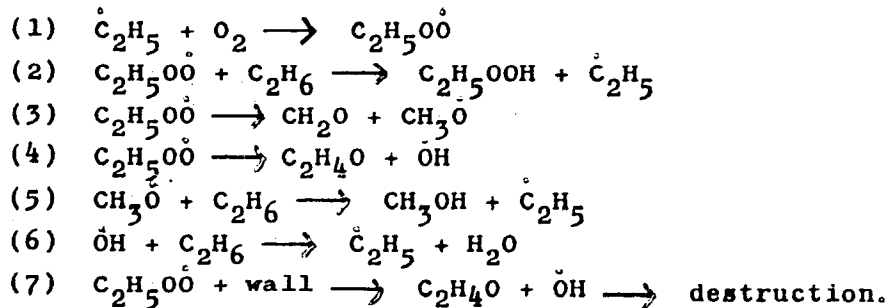
**TEXT:** Using the apparatus described by the present authors in a previous article (Ref.1: Izv. AN ArmSSR, KhN, v.14, no.6, 517 (1961)) the authors investigated the oxidation of ethane up to 400 °C. It was established that the reaction products up to 150 °C are ethyl hydroperoxide and acetaldehyde. Above this temperature the compounds are formed together with formaldehyde and methyl alcohol. It was shown that the rate at which the concentration of ethylperoxide increases with temperature passes through a maximum at 270-280 °C and approaches zero at 350-360 °C. The rate of formation of acetaldehyde does not change to 150 °C and increases with temperature above 150 °C. The rates of

Card 1/3

4

Photochemical oxidation of ethane ... S/171/61/014/006/002/005  
E075/E136

formation of formaldehyde and methyl alcohol increase with temperature. The ethyl peroxide radical was shown to be able to isomerise at the C—H bond in the presence of C—C bond and to decompose with the formation of acetaldehyde and OH radical. Departing from the generally accepted scheme for gaseous oxidation of hydrocarbons, the authors postulate on the basis of the results obtained the following mechanism of the reaction:



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Photochemical oxidation of ethane ... S/171/61/014/006/002/005  
E075/E136

This mechanism differs from those generally accepted by the elementary reaction (4) and the form of notation for reaction (7) corresponding to destruction of the peroxide radical. V.S. Pudov is thanked for the chromatographic analysis of the products, and B.V. Rozanov for the spectral one. There are 6 figures.

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

SUBMITTED: December 19, 1961

Card 3/3



NALBANDYAN, A.B.; GULEN', I.I.

Determining the velocity constant of the reaction  $H + CH_4 \rightleftharpoons H_2 + CH_3$ . Dokl. Akad. Nauk SSSR 33 no.3:49-52 '61.

(MIRA 14:10)

1. Institut Khimicheskoy Fiziki AN SSSR. 2. Chlen-korrespondent AN Arzyanskoy SSR (Zor Nalbandyan).

(Methane)  
(Hydrogen)  
(Oxidation)

SOKOLOVA, N.A.; MARKEVICH, A.M.; NALBANDYAN, A.B. (Moskva)

Initiating stage in the oxidation of acetaldehyde. Zhur. fiz.  
khim. 35 no. 4:850-857 Ap '61. (MIRA 14:5)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki.  
(Acetaldehyde) (Oxidation)

KARMILOVA, L.V.; YENIKOLOPYAN, N.S.; NALBANDYAN, A.B.

Kinetics and mechanism of methane oxidation. Part 4: Effect  
of hydrogen peroxide and water on the reaction kinetics.  
Zhur. fiz. khim. 35 no.5:1046-1053, My '61. (MIRA 16:7)

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

KARMILOVA, L.V.; YENIKOLOPYAN, N.S.; NALBANDYAN, A.B.; IL'IN, V.T.  
(Moskva)

Kinetics and mechanism of methane oxidation. Part 5:  
Constant rate of methane oxidation. Zhur. fiz. khim.  
35 no.7:1435-1442 J1 '61. (MIRA 14:7)

1. Akademiya nauk SSSR, Institut khimicheskoy fiziki.  
(Methane) (Oxidation)

S/020/61/139/005/016/021  
B103/B220

AUTHORS: Gorban', N. I., Azatyan, V. V., and Malbandyan, A. B.

TITLE: Determination of the recombination coefficient of oxygen atoms on the surface of quartz covered by potassium tetraborate

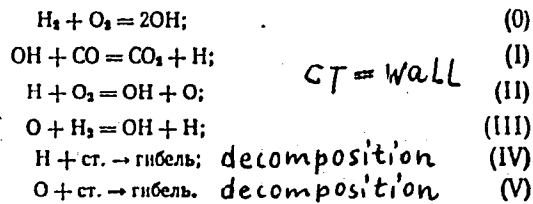
PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 5, 1961, 1141-1144

TEXT: A new method of determining the recombination coefficient of oxygen atoms is suggested, since the methods used so far (W. V. Smith, J. Chem. Phys., 11, 3, 110 (1943); J. W. Linnet, Trans. Farad. Soc., 55, 8, 1323 (1959) and others) are inadequate. The authors selected a system in which the concentration of O atoms is at least commensurable with that of H atoms, to study the effectivity ( $\xi_0$ ) of heterogeneous recombination of oxygen atoms by measuring the inflammation limits. In such a system, the branching process of the chains should be dependent on the reaction rate of atomic oxygen. Such a system with a well-known reaction mechanism is the low-temperature combustion of CO in the presence of small admixtures of H<sub>2</sub>. The authors present the following equation for the mechanism of this reaction in the neighborhood of the first inflammation limit:

Card 1/6

Determination of the recombination ...

S/020/61/139/005/016/021  
B103/B220



Therefrom the following equation is derived:

$$(O_2)^{CO} = [(k_4)^{CO}/2k_2] [1 + (k_5)^{CO}/k_3(H_2)] \quad (1),$$

where  $(O_2)^{CO}$  and  $(H_2)^{CO}$  are the oxygen and hydrogen concentrations at the first inflammation limit:  $k_i$  are the rate constants of the reactions concerned. The superscripts indicate that the values refer to CO-O<sub>2</sub> mixtures with small admixtures of H<sub>2</sub>. If

reactions of heterogeneous chain rupture occur in the kinetic range,  $k_4$  and  $k_5$  are independent of the composition of the mixture. Neglecting the indices of these constants and replacing, in (1), the concentrations by partial pressures one obtains:

Case 2/4

Determination of the recombination ...

S/O20/61/139/005/016/021  
B103/B220

$$p_{O_2}^{CO} = \left[ k_4 T / 2k_2 \cdot 10^{19} \right] (1 + k_5 T / k_3 \cdot 10^{19} \cdot p_{H_2}^{CO}) \quad (2).$$

If reactions (IV) and (V) proceed in the kinetic range, it follows from (2) that the dependence of  $p_{O_2}^{CO}$  on  $1/p_{H_2}^{CO}$  at constant temperature is linear. The straight line

$$\text{representing this function cuts the ordinate in: } b = k_4 T / 2k_2 \cdot 10^{19} \quad (3);$$

Here,  $\tan \alpha = (k_4 T / 2k_2 \cdot 10^{19}) \left[ (k_5 T / k_3 \cdot 10^{19}) k_3 \right] \quad (4)$  is valid. Thus, it is possible to determine  $\tan \alpha$  and  $b$  by measuring the initial inflammation limits of CO-O<sub>2</sub> mixtures (with small admixtures of H<sub>2</sub>) at various temperatures.

Based on the known value of  $k_3$ ,  $k_5$  can be determined from (4). The coefficient ( $\mathcal{E}_0$ ) is derived from  $k_5 = \mathcal{E}_0 v_0 / d \quad (5)$ , where  $v_0$  is the thermal velocity of O atoms, and  $d$  is the diameter of the vessel. If  $\mathcal{E}_0 = \mathcal{E}_0^c e^{-E_5/RT}$  in the temperature range studied, the equation

$$\log \tan \alpha / b T^{1.5} = \log k_5^0 / k_3^0 \cdot 10^{19} + (E_3 - E_5) / 2.3RT \quad (6)$$

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from (3) and (4) and from  $v_0$ . Here,  $k_5^0 = \xi_0^0 \sqrt{8R/\pi m_5} / d$  (7). According to (6), a linear relation must exist in this case between  $\log \tan \alpha / bT^{1.5}$  and  $1/T$ .  $E_5$  can be determined from the slope of the straight line and from the known value of  $E_3$ , whereas  $\xi_0^0$  can be calculated from the initial ordinate  $\log k_5^0 / k_3^0 \cdot 10^{19}$ . The tests were made in a quartz vessel lined with potassium tetraborate. The inner surface was treated repeatedly by inflammations of  $O_2$ - $H_2$  mixture before the measurements were carried out. Thereby, the limit was reduced to a constant value. For the test methods see: N. I. Gortan', A. B. Nalbandyan, DAN, 132, no. 6 (1960). The inflammation limits were measured at 550-640°C. The mixtures contained 2CO +  $O_2$ , and 1.95 and 4.0% of  $H_2$ , respectively. The mixture  $2H_2 + O_2$  contained 6% of  $H_2$ . The measured values of the limits were less than 1/100 of the limits found in a vessel lined with MgO, in which MgO guaranteed the proceeding of (IV) and (V) in the diffusion range. Both the low inflammation limits of  $H_2$ - $O_2$  and CO- $O_2$  mixtures and the dependence of the values of these limits on the

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surface condition prove that (IV) and (V) take place in the kinetic range. Since

$k_4/2k_2 = [O_2]^{H_2}$ , where  $[O_2]^{H_2}$  is the  $O_2$  concentration at the first inflammation limit of the  $H_2-O_2$  mixture, the right side of Eq. (3) may be replaced by  $p_{O_2}^{CO}$ . This means that the section which is cut off by the straight line

$p_{O_2}^{CO} - 1/p_{H_2}^{CO}$  on the ordinate equals the partial pressure of oxygen at the first inflammation limit of a  $H_2-O_2$  mixture. The correctness of Eq. (1) was found graphically owing to the dependence of  $p_{O_2}^{CO}$  on  $1/p_{H_2}^{CO}$  and confirmed

experimentally. The value of  $E_3 - E_5$  was calculated from the slope of the straight line on the basis of (6) and is  $5.6 \pm 0.2$  kcal/mole. Since  $E_3$  is  $11.7 \pm 0.7$  kcal/mole,  $E_5 = 6.1 \pm 1.0$  kcal/mole. On the basis of (6) and (7)  $E_0^c$  was calculated from b and  $k_3 = 1.1 \cdot 10^{-10}$  cm<sup>3</sup>/molecule·sec and was

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$1.65 \cdot 10^{-2} \text{ sec}^{-1}$ . Consequently,  $\xi_0 = 1.65 \cdot 10^{-2} e^{-(6100 \pm 1000)/RT_{\text{sec}^{-1}}}$  in the temperature range studied.  $\xi_H$  (recombination coefficient of H atoms on the wall of the vessel) was calculated from the graphically obtained values of  $b$  and from  $k_2$  by using an equation analogous to (5):

$\xi_H = 9 \cdot 10^{-14} e^{-(5400 \pm 1000)/RT}$ . The latter values are in good agreement with those of A. B. Nalbandyan and S. M. Shubina (ZhFKh, 20, 1249 (1946)), and N. N. Semenov (O nekotorykh problemakh khimicheskoy kinetiki i reaktsionnoy sposobnosti (Some problems of chemical kinetics and reactivity), Izd. AN SSSR, 1958)). There are 3 figures and 16 references: 9 Soviet and 7 non-Soviet.

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

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AUTHORS: Azatyan, V. V., Akopyan, L. A., Nalbandyan, A. B., and Ozherel'iyev, B. V.

TITLE: Detection of oxygen atoms in the rarified flame of carbon monoxide in oxygen in the presence of small hydrogen admixtures

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 1, 1961, 129 - 130

TEXT: The authors discuss the problem of detecting free atoms in CO combustion at low temperatures with small H<sub>2</sub> admixtures as catalyst. For this purpose, the method of electron paramagnetic resonance was used. To avoid a recombination of atoms into molecules, the test tube was washed with hydrofluoric acid and distilled water, and finally covered with a layer of potassium tetraborate. For several days, a CO and O<sub>2</sub> flame containing H<sub>2</sub> admixtures was passed through the tube. By this process a 600 - 650°C flame was obtained at pressures of up to 1.5 - 2 mm Hg. The tests were conducted with stoichiometric amounts of CO and CO<sub>2</sub> containing  
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up to 7% of H<sub>2</sub>, at a volume rate of 82 cm<sup>3</sup>/min (linear rate  $\approx$  18 m/sec), and a pressure of 5.5 mm Hg. The temperature varied between 607 and 650°C. Under these conditions, an epr signal of atomic O consisting of one component was determined, with a g factor of 1.5. The value of the g factor is in agreement with that published for atomic oxygen. The concentration determinations of atomic O and H were conducted simultaneously. The dependence of the concentration of atomic H and O on that of H<sub>2</sub> contained in the CO - O<sub>2</sub> mixture, was also determined at 610°C. The measured values show that the concentration of O atoms is commensurable with that of H atoms, and that the two concentrations increase as the H<sub>2</sub> content increases. The ratio O/H decreases from 4.5 to 0.9 with an increase of the H<sub>2</sub> content from 1.1 to 6.9 %. A temperature increase from 607 to 650°C at an H<sub>2</sub> content of 3.8 % causes a concentration increase of atomic O and H from  $2.9 \cdot 10^{14}$  to  $4.1 \cdot 10^{14}$  particles/cm<sup>3</sup>, and from  $4.6 \cdot 10^{14}$  to  $7.8 \cdot 10^{14}$  particles/cm<sup>3</sup>, respectively. The results show that the sum of partial pressures

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