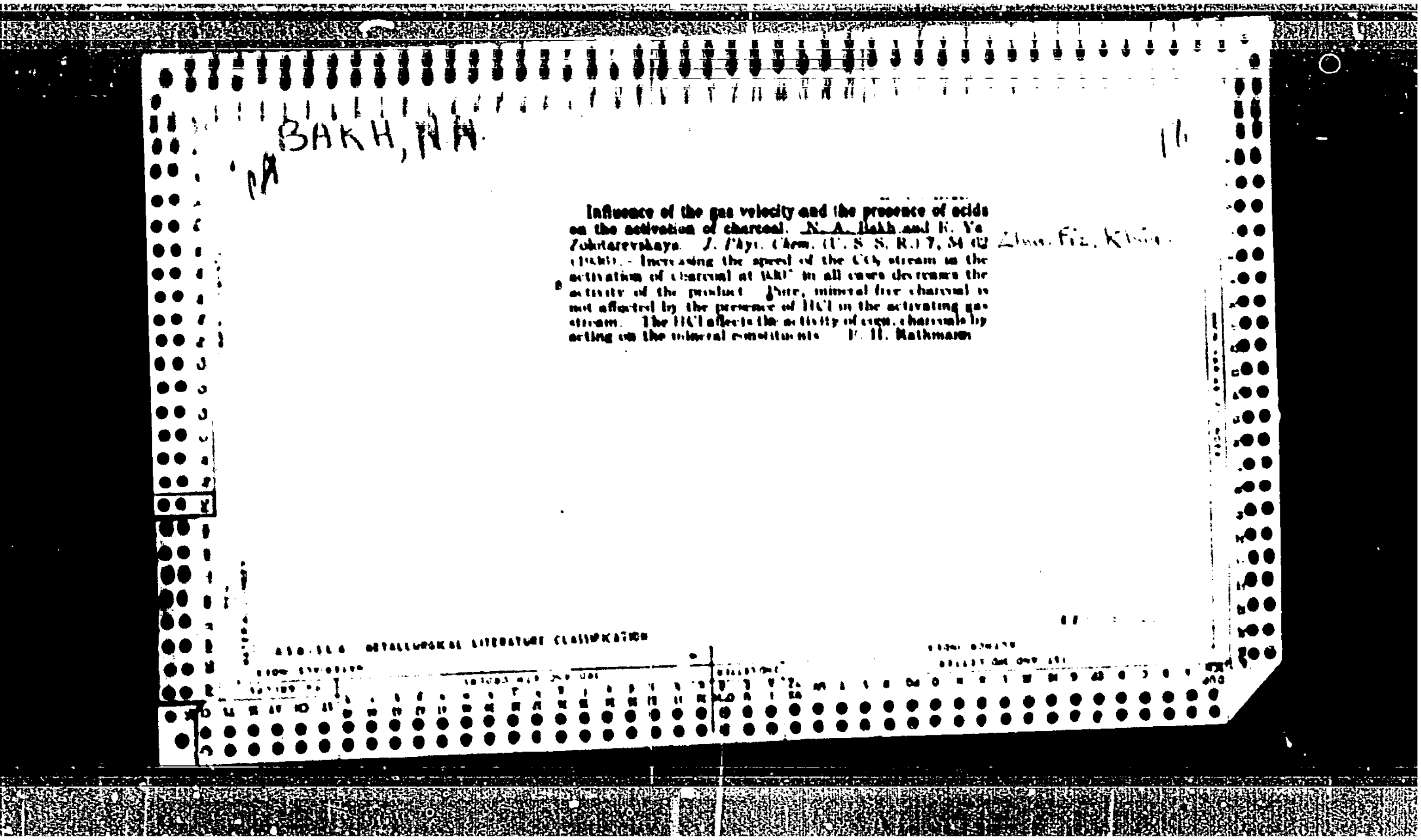


BAKH, N.A.

Influence of the gas velocity and the presence of acids on the activation of charcoal. N. A. Bakh and E. Ya. Zolotarevskaya. J. Phys. Chem. (U. S. S. R.) 7, 54 (1936).—Increasing the speed of the CO_2 stream in the activation of charcoal at 900° in all cases decreases the activity of the product. Pure, mineral free charcoal is not affected by the presence of HCl in the activating gas stream. The HCl affects the activity of com. charcoals by acting on the mineral constituents. F. H. Rathmann

Zhur. Fiz. Khim.

METALLURGICAL LITERATURE CLASSIFICATION

BACH, N.A.

A 54 B

/N

4268. Electrochemistry of Platinum Sols. Part II. Nathalie Bach and A. Rabov. *Acta Physicochimica*, 7, 1, pp. 85-94, 1937. *In English.*—Pt sols of various concentrations, prepared by arcing Pt in an atmosphere of H_2, O_2 or air at different temperatures, were coagulated by means of freezing and remelting. In the case of H_2-Pt-sols, the liquid obtained by melting the frozen sol is identical with the intermicellar liquid. The difference between its conductivity and that of the sol corresponds to the colloid's own conductivity; this difference increased with the concentration of the sol and reached 75% of the total conductivity when the concentration was 900 mg./l. Pt sols prepared in an atmosphere of H_2 consist of Pt particles and H ions, forming the diffuse part of the double layer. In the case of O_2-Pt-sols the difference between the conductivity of the coagulated and original sols is constant at all concentrations; it cannot be interpreted as the colloid's own conductivity, because of the presence of electrolytes. Air-Pt-sols are similar to O_2-Pt-sols, but their structure is still more complicated. [For Part I see Abstract 4787 (1935).] AUTHORS.

A S M - S L A METALLURGICAL LITERATURE CLASSIFICATION

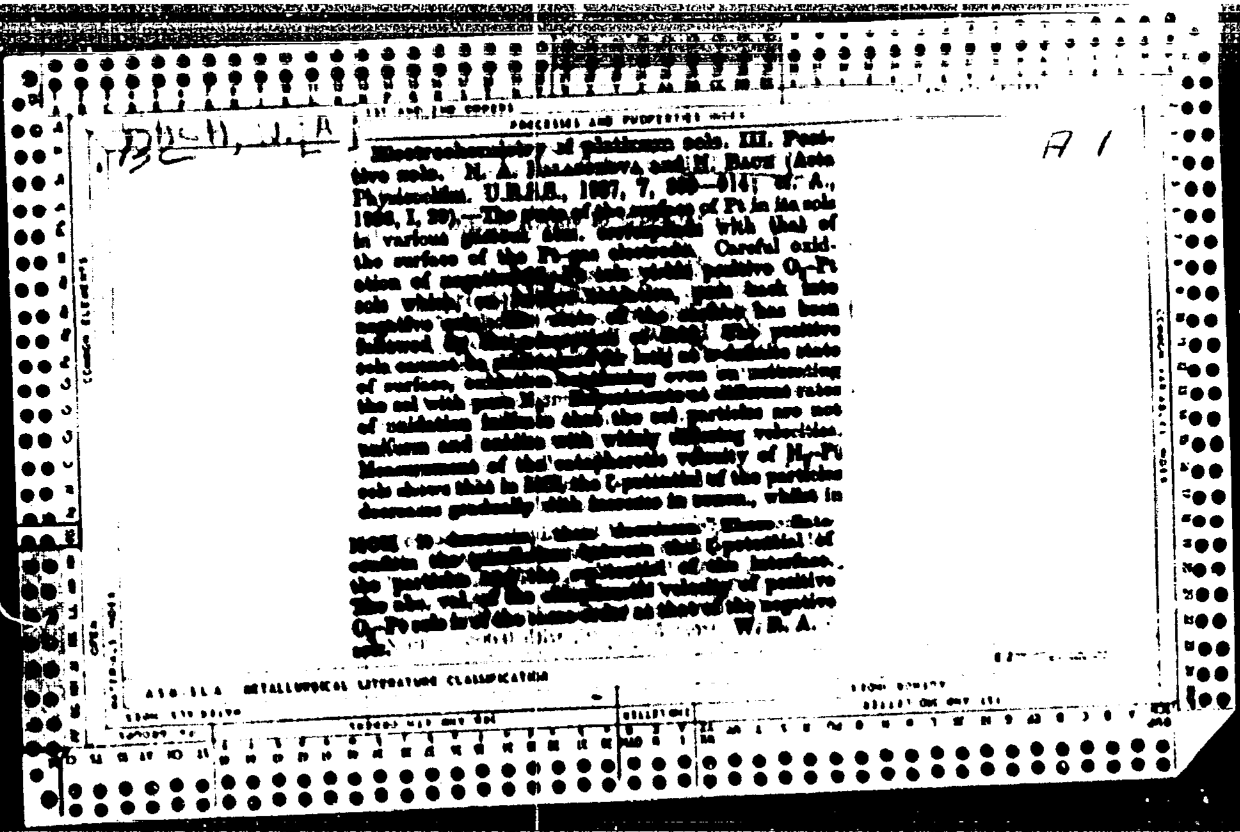
PROCESSES AND PROPERTIES INDEX

BAKH, N.A.

2

Reversal of the sign of charge of activated charcoal in an atmosphere of oxygen. N. A. Bakh and V. Zimin. Acta Physicochim. U.R.S.S. 7, 151-8(1937)(in English); cf. C. A. 27, 5607. The reversal of sign of pure charcoal in dil. alk. soln. in air is due to the formation of surface oxides. If the possibility of this oxidation is eliminated, no reversal of sign is observed. The charcoal remains positive when treated with O at room temp. either as a dry powder or as a suspension in H_2O. W. George Parks

ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION



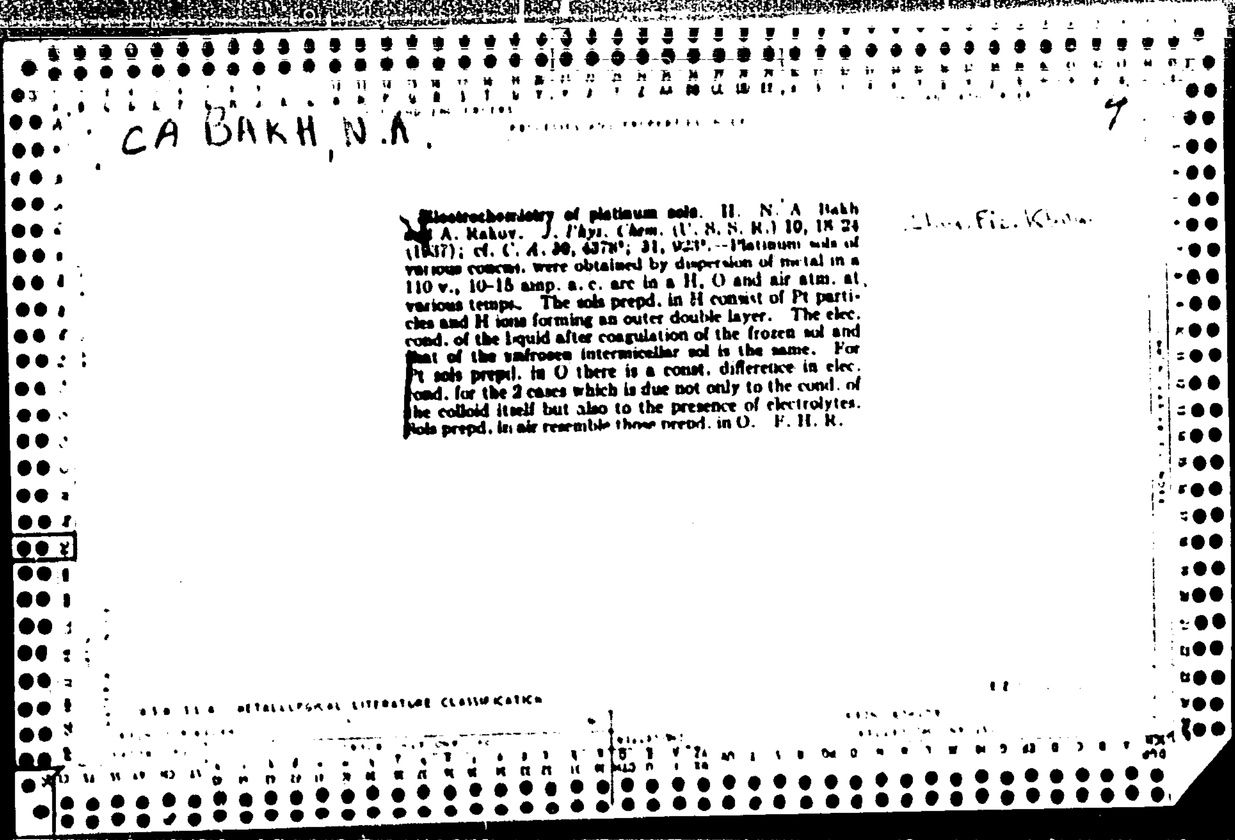
BACH, N. A.

A 1

PROCESSES AND PROPERTIES INDEX

Electrochemistry of platinum sols. III. Positive sols. N. A. Balashova and N. Bach (Acta Physicochim. U.R.S.S., 1937, 7, 899—914; cf. A., 1936, I, 29).—The state of the surface of Pt in its sols in various [illegible] with that of the surface of the Pt-gas electrode. Careful oxidation of [illegible] sols yields positive O-Pt sols which, [illegible], pass back into negative [illegible] state of the [illegible] has been followed [illegible] positive sols [illegible] of surface, [illegible] even on [illegible] the sol with pure H_2. [illegible] different rates of oxidation indicate that the sol particles are not uniform and oxidise with widely differing velocities. Measurement of the cataphoretic velocity of H_2-Pt sols shows that in HCl the ζ-potential of the particles decreases gradually with increase in concn., whilst in NaOH [illegible] confirm the [illegible] between the ζ-potential of the particles and the [illegible] potential of the interface. The abs. val. of the cataphoretic velocity of positive O-Pt sols is of the same order as that of the negative sols. W. R. A.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



CA BAKH, N.A.

7

Zhur. Fiz. Khim.

Electrochemistry of platinum sols. II. N. A. Bakh and A. Rakov. J. Phys. Chem. (U. S. S. R.) 10, 18-24 (1937); cf. C. A. 30, 4378^{9}; 31, 923^{9}.—Platinum sols of various concns. were obtained by dispersion of metal in a 110 v., 10-15 amp. a.c. arc in a H, O and air atm. at various temps. The sols prepd. in H consist of Pt particles and H ions forming an outer double layer. The elec. cond. of the liquid after coagulation of the frozen sol and that of the unfrozen intermicellar sol is the same. For Pt sols prepd. in O there is a const. difference in elec. cond. for the 2 cases which is due not only to the cond. of the colloid itself but also to the presence of electrolytes. Sols prepd. in air resemble those prepd. in O. F. H. R.

METALLURGICAL LITERATURE CLASSIFICATION

BAKH, N. A.

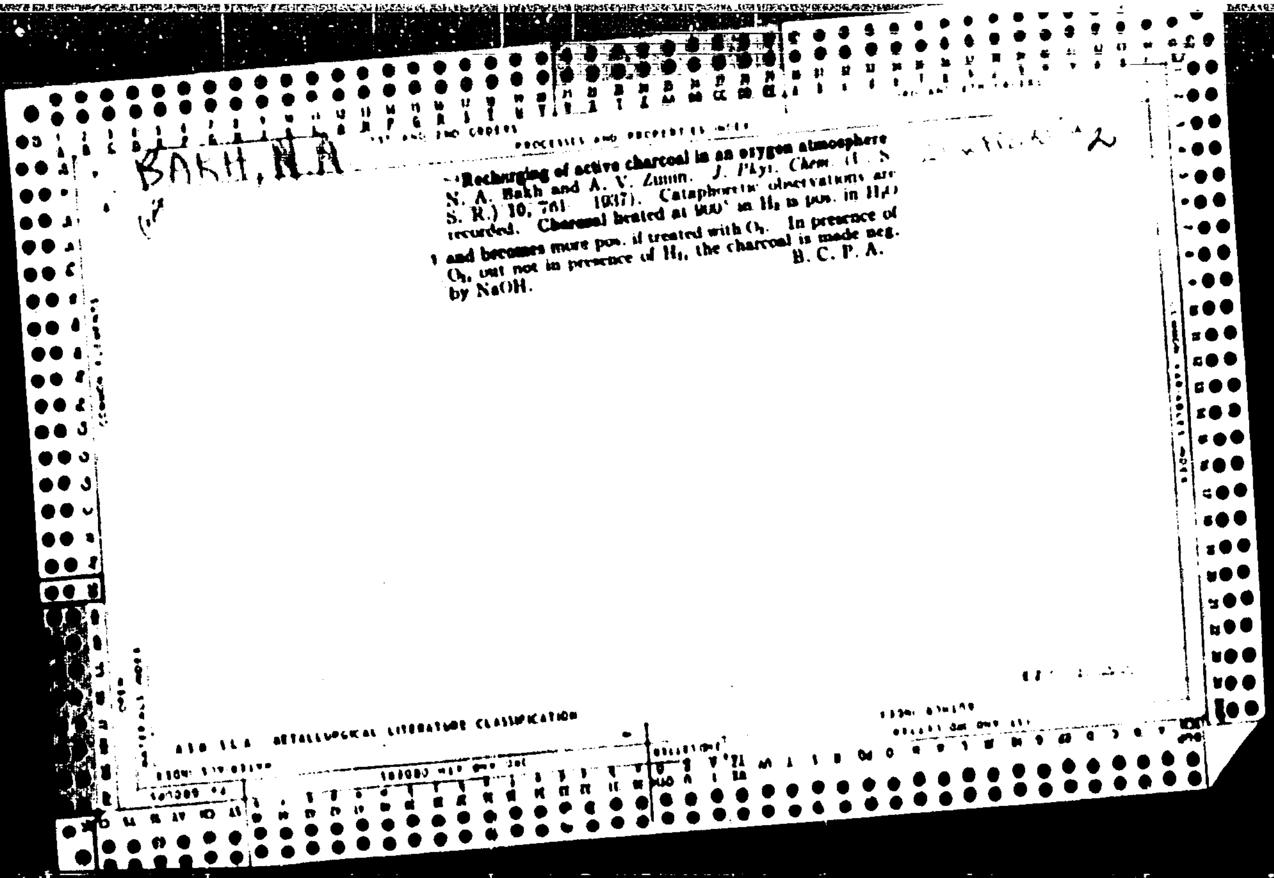
CA

Zhur.Fiz.Khim.

Electrochemistry of platinum sols. III. N. A. Balashova and N. A. Bakh. *J. Phys. Chem.* (U.S.S.R.) 10, 575-80(1937); cf. C. A. 32, 441⁹. Pos., oxidized Pt sols were prepd. from neg. H_2-Pt sols by passing a slow stream of very dil. O_2 (less than 1% in N_2) through a 0.01 N HCl or H_2SO_4 suspension of the sol until max. adsorption of acid occurred. These pos., oxidized Pt sols are not stable and slowly change to neg. O_2-Pt sols. The cataphoretic velocities of pos. and neg. sols are opposite but equal in abs. value. From the different oxidation velocities of pos. H_2-Pt sols it follows that the individual particles are not of like size and oxidize at various rates. The change of cataphoretic velocity with concn. shows that the ζ potential decreases with increasing acid concn. while in KOH it first increases and then decreases. ζ and ε potential are therefore parallel phenomena.

E. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



BAKH, N.A.

PROCESSES AND PROPERTIES INDEX

Recharging of active charcoal in an oxygen atmosphere. N. A. Bakh and A. V. Zunin. *J. Phys. Chem.* (U. S. S. R.) 10, 761 (1937). Cataphoretic observations are recorded. Charcoal heated at 900° in H_2 is pos. in H_2O and becomes more pos. if treated with O_2. In presence of O_2, but not in presence of H_2, the charcoal is made neg. by NaOH.

B. C. P. A.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

BAKH, N.A.

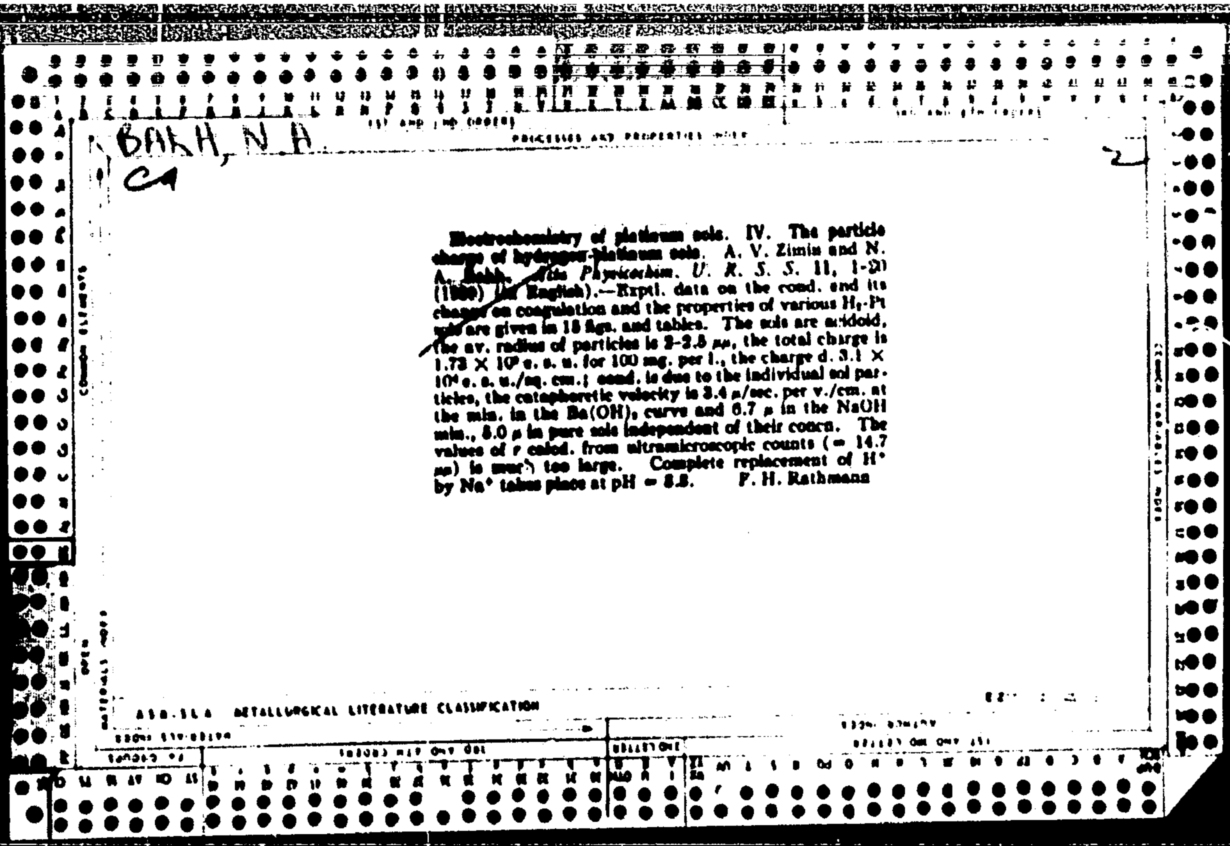
Ca

2)

ELECTROKINETIC POTENTIAL AT GAS-LIQUID INTERFACES. I. CATAPHORETIC VELOCITY OF GAS BUBBLES IN SOLUTIONS OF INORGANIC ELECTROLYTES. N. Bakh and A. Gilman. Acta

Physikochim. U. R. S. S. 9, 1-20(1938).—The true cataphoretic velocity v of H bubbles in H_2O (I), and in aq. KCl (II) and aq. $ThCl_4$ (III) was detd. by a method which takes into account the electroosmotic flow of the liquid in a cell. In I and II the charge on the bubbles is neg. and v corresponds with a ζ-potential of about -30 mv. In III the charge on the bubble remains neg. at all concns. up to 10^{-5} N, and the apparent reversal of charge at 10^{-4} N is caused by the carrying away of bubbles by H_2O, which moves toward the cathode with a velocity greater than that with which the bubbles move toward the anode. v_{II} approximates v_I and v_{III}. Changes in KCl concn. and $ThCl_4$ concn. have little effect on v. H

Cataphoresis of gas bubbles in solutions of capillary-active organic electrolytes. A. Gilman and N. Bakh. *Ibid.* 27-36. The bubble has a pos. charge in aq. NH_4Cl and $N(C_4H_9)_4Cl$ at concns. (c) of more than 10^{-4} mol. per l. The ζ potential (and hence v) is approx. proportional to log c. The ratios of NH_4Cl concn. and $N(C_4H_9)_4Cl$ concn. which correspond with the same effects are const. and ≈ 0. Na palmitate gives the bubble a neg. charge which increases with concn.; the ζ-potential also increases at the liquid-glass interface. H. C. P. A.



BAKH, N.A.

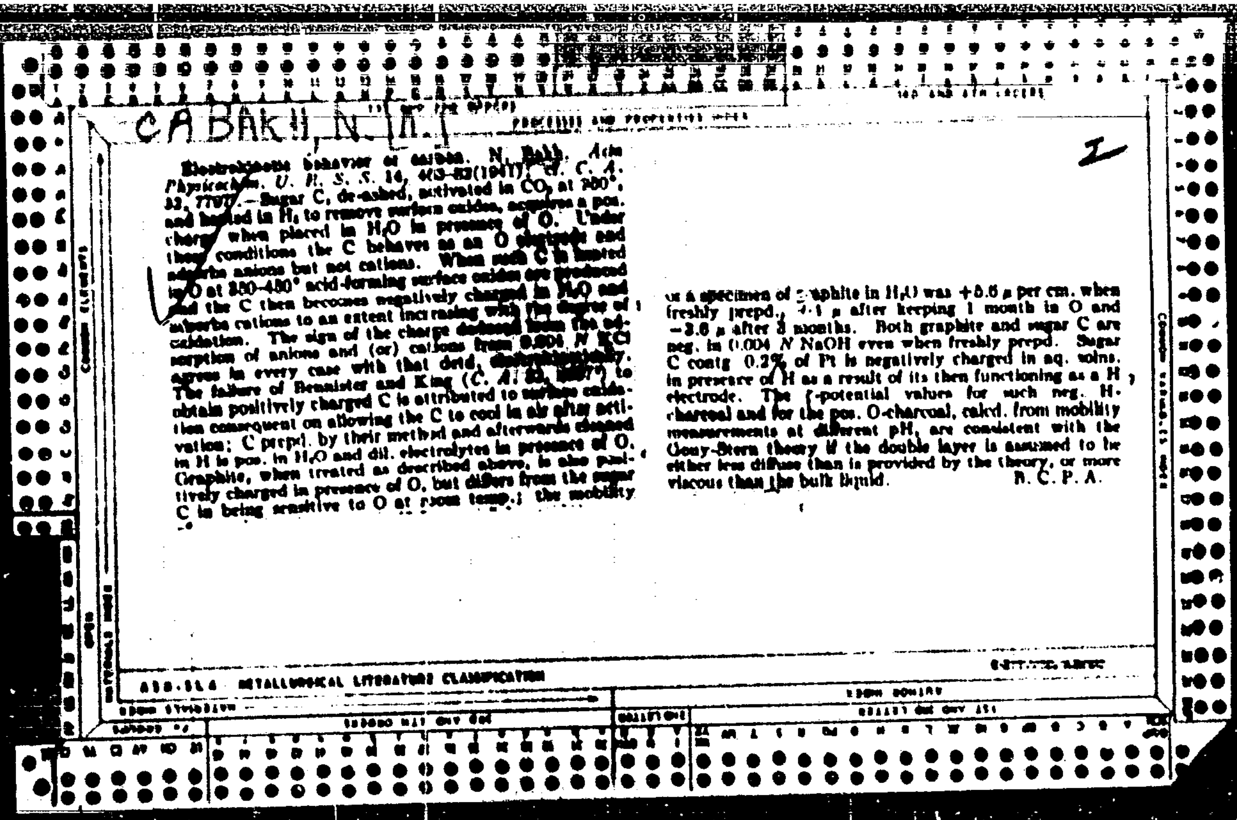
CA

2

PROCESSES AND PROPERTIES INDEX

Electrochemistry of platinum sols. IV. The particle charge of hydrogen-platinum sols. A. V. Zimin and N. A. Bakh. *Acta Physicochim. U. R. S. S.* 11, 1-20 (1939) (in English).—Exptl. data on the cond. and its change on coagulation and the properties of various H_2-Pt sols are given in 15 figs. and tables. The sols are acidoid, the av. radius of particles is 2-2.5 μμ, the total charge is 1.73 × 10^{9} e. s. u. for 100 mg. per l., the charge d. 3.1 × 10^{4} e. s. u./sq. cm.; cond. is due to the individual sol particles, the cataphoretic velocity is 3.4 μ/sec. per v./cm. at the min. in the $Ba(OH)_2$ curve and 6.7 μ in the NaOH min., 5.0 μ in pure sols independent of their concn. The values of r calcd. from ultramicroscopic counts (= 14.7 μμ) is much too large. Complete replacement of H^+ by Na^+ takes place at pH = 8.8. F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



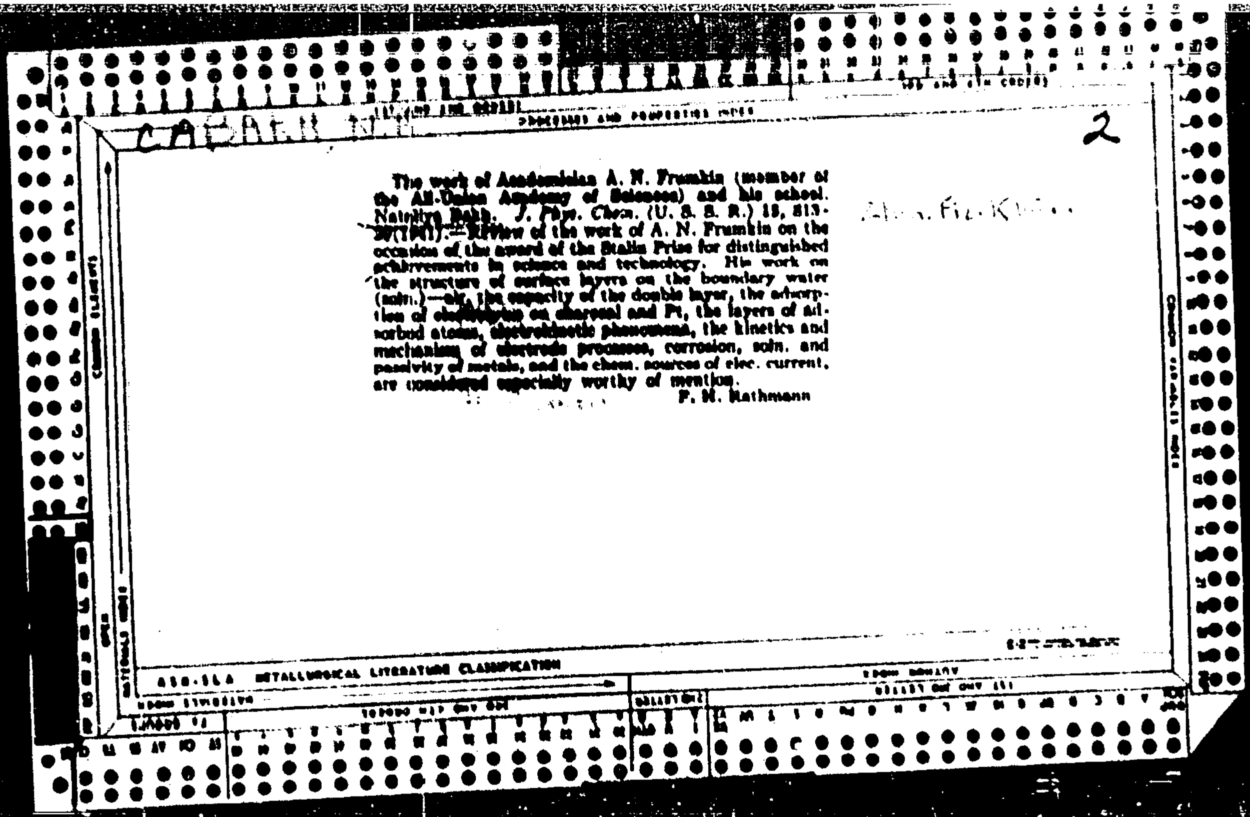
CABAKH, N. П.

PROCESSES AND PROPERTIES INDEX

1

Electrokinetic behavior of carbon. N. Bach. *Acta Physicochim. U. R. S. S.* 14, 463-82(1941); cf. *C. A.* 33, 7707.—Sugar C, de-ashed, activated in CO_2 at 900°, and heated in H_2 to remove surface oxides, acquires a pos. charge when placed in H_2O in presence of O. Under these conditions the C behaves as an O electrode and adsorbs anions but not cations. When such C is heated in O at 350-450° acid-forming surface oxides are produced and the C then becomes negatively charged in H_2O and adsorbs cations to an extent increasing with the degree of oxidation. The sign of the charge deduced from the adsorption of anions and (or) cations from 0.001 *N* KCl agrees in every case with that detd. electrophoretically. The failure of Bennister and King (*C. A.* 33, [illegible]) to obtain positively charged C is attributed to surface oxidation consequent on allowing the C to cool in air after activation; C prepd. by their method and afterwards cleaned in H is pos. in H_2O and dil. electrolytes in presence of O. Graphite, when treated as described above, is also positively charged in presence of O, but differs from the sugar C in being sensitive to O at room temp.; the mobility of a specimen of graphite in H_2O was +5.6 μ per cm. when freshly prepd., +1 μ after keeping 1 month in O and −3.6 μ after 3 months. Both graphite and sugar C are neg. in 0.004 *N* NaOH even when freshly prepd. Sugar C contg. 0.2% of Pt is negatively charged in aq. solns. in presence of H as a result of its then functioning as a H electrode. The ζ-potential values for such neg. H-charcoal and for the pos. O-charcoal, calcd. from mobility measurements at different pH, are consistent with the Gouy-Stern theory if the double layer is assumed to be either less diffuse than is provided by the theory, or more viscous than the bulk liquid. R. C. P. A.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION



PROCESSES AND PROPERTIES INDEX

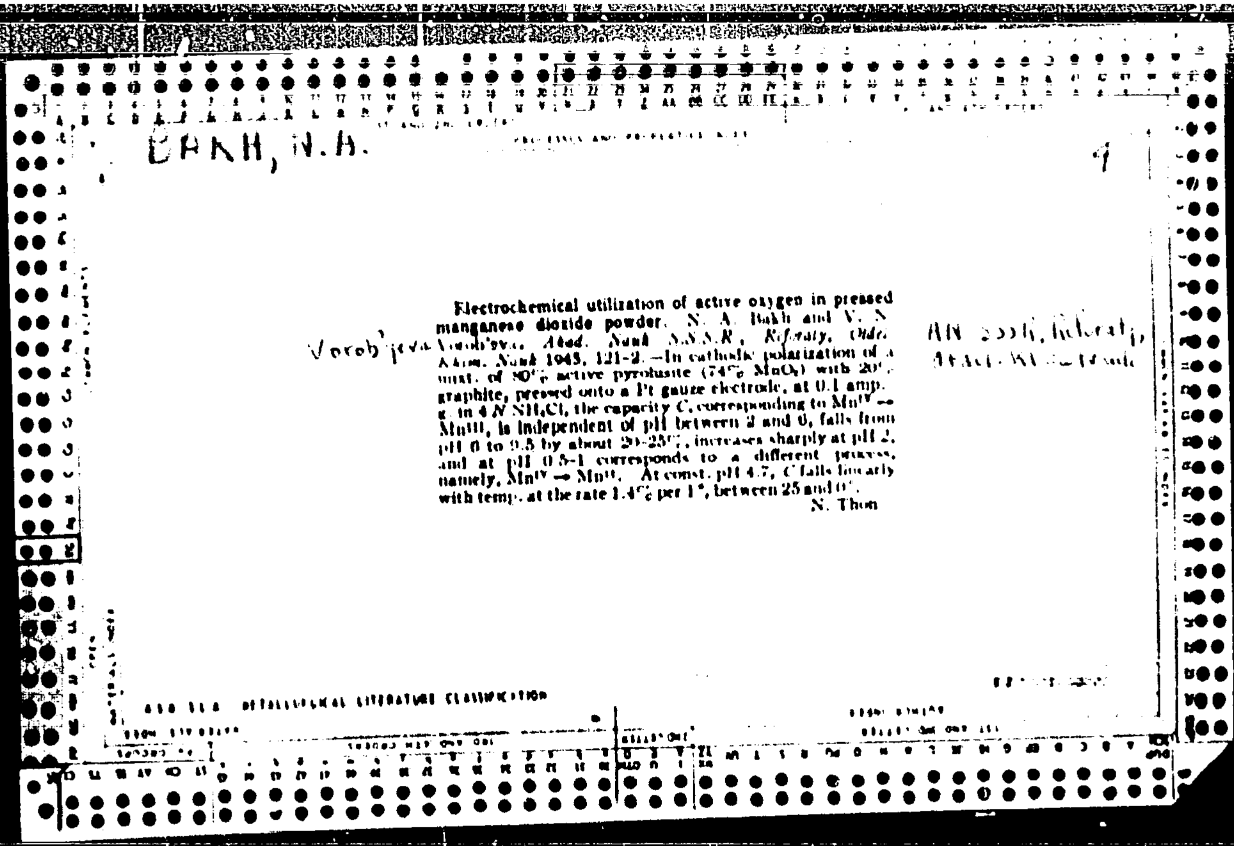
2

The work of Academician A. N. Frumkin (member of the All-Union Academy of Sciences) and his school. Natalya Bakh. *J. Phys. Chem.* (U. S. S. R.) 15, 813-20(1941).—Review of the work of A. N. Frumkin on the occasion of the award of the Stalin Prize for distinguished achievements in science and technology. His work on the structure of surface layers on the boundary water (soln.)—air, the capacity of the double layer, the adsorption of electrolytes on charcoal and Pt, the layers of adsorbed atoms, electrokinetic phenomena, the kinetics and mechanism of electrode processes, corrosion, soln. and passivity of metals, and the chem. sources of elec. current, are considered especially worthy of mention.

F. H. Rathmann

Al.-. Frumkin

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



BAKH, N.A.

PROCESSES AND PROPERTIES INDEX

4

Electrochemical utilization of active oxygen in pressed manganese dioxide powder. N. A. Bakh and V. S. Vorob'eva. *Akad. Nauk S.S.S.R., Referaty, Otdel. Khim. Nauk* 1945, 121-2.—In cathodic polarization of a mixt. of 80% active pyrolusite (74% MnO_2) with 20% graphite, pressed onto a Pt gauze electrode, at 0.1 amp. g. in 4 *N* NH_4Cl, the capacity C, corresponding to $Mn^{IV} \rightarrow Mn^{III}$, is independent of pH between 2 and 6, falls from pH 6 to 9.5 by about 20-25%, increases sharply at pH 2, and at pH 0.5-1 corresponds to a different process, namely, $Mn^{IV} \rightarrow Mn^{II}$. At const. pH 4.7, C falls linearly with temp. at the rate 1.4% per 1°, between 25 and 0°.

N. Thon

Vorob'jeva

AN SSSR, Referaty,
Otdel. Khim. Nauk

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

BAKH, N.A.

The Work of Russian Investigators in the Field of Chemical Sources of Current in the Second Half of the XIXth Century. N. A. Bakh (*Trudy Soveshchaniya po Elektrokhimii 1950*, 1953, 532-538).—(In Russian). An historical review. 23 ref.
—G. V. E. T.

BAKH, Nataliya

[Radiolytic oxidation of organic compounds] Radioliticheskoe okislenie organicheskikh soedinenii. Moskva, 1955. 21 p.
(MIRA 14:6)

(Radiochemistry) (Oxidation)
(Organic compounds)

a paper presented a t the Atoms for Peace Conference, Geneva, Switzerland, 1955.

BAKH, N.A., professor, doktor khimicheskikh nauk, redaktor; VERESHCHINSKIY, I.V., redaktor; DOLIN, P.I., redaktor; MYASNIKOV, I.A., redaktor; KISELEVA, A.A., tekhnicheskiy redaktor.

[Collection of papers on radiation chemistry] Sbornik rabot po radiatsionnoi khimii. Moskva, 1955. 262 p. (MLRA 8:11)

1. Akademiya nauk SSSR.
(Radiation)

BAKH NA

BAKH, N.A

7718

ACTION OF IONIZING RADIATIONS ON AQUEOUS SOLU- CH
TIONS OF INORGANIC SALTS. N A Bakh., p.33-40 in
Meetings of the Division of Chemical ~~Sciences~~ Session of
the Academy of Sciences of the U.S.S.R. on the Peaceful Use
of Atomic Energy, July 1-5 1955 Moscow Publishing
House of the Academy of Sciences of the U S S R 1955
378p. (In Russian)

The influence of various factors (concentration, pH,
dissolved gases) on the yields of products and the establish-
ment of steady state conditions has been studied in irradiated
solutions of ferrous and ferric salts potassium iodide, and
sodium nitrate The relation between the establishment of a
steady state in the liquid phase and the evolution of gas is
discussed. Either total absence of gas evolution at steady
state conditions or evolution of $2H_2 + O_2$ mixtures with
constant yield is shown to prevail in different ferrous and
ferric salt solutions. It is suggested that the ability of the
solute to decompose H_2O_2 in a catalytic not radiation induced
process (e. g., Fe^{2+}, J^-, Br^--ions) plays an important part
in the evolution of $2H_2 + O_2$ gas upon radiolysis of aqueous
solutions. NO_2^--ions and H_2O_2 are shown to be formed in
irradiated NaNO₃ solutions with almost equal yields [illegible]
[illegible]
per [illegible] in alkaline 1M solutions. Such [illegible] cannot be
accounted for if only H and OH radicals due to primary
ionization are considered. Measurement of the redox
potential during irradiation shows that besides NO_2^--ions
and H_2O_2 other products of higher reducing power appear in
the solution [illegible] considering reaction
mechanisms [illegible] possible reactions
both radiation [illegible] must be taken into
account. (auth)

5

The measurement of the oxidation-reduction potential of systems during radiation. V. I. Medvedovskii, N. A. Bakh, and E. V. Zhuravskaya. *Sbornik Rabot Radiatsionnoi Khim., Akad. Nauk S.S.S.R.* 1955, 71-8.—An app. is described for the measurement of the potential of solns. irradiated by Röntgen tubes at 70 kv. and 150 ma. with beam vertically upward. A looped Pt-wire electrode (1 mm. in diam.) was rotated (60-3000 r.p.m.). The power (measured by the ferrous sulfate dosimetric method) was 2.7 × 10^{16} e.v./cc.-sec. Solns. of 0.8*N* H_2SO_4 contg. 0.0 × 10^{-4} moles/l. Fe^{++}, and 0.012 × 10^{-4} moles/l. Fe^{+++} were irradiated, and the potential of the system followed until the Fe^{++} concn. was 0.13 × 10^{-4} moles/l. and the Fe^{+++} concn. was 5.95 × 10^{-4} moles/l. In all cases, the measured potential agreed closely with the standard (unirradiated) solns. of corresponding concns. and appeared to be a function primarily of the ratio $[Fe^{+++}]/[Fe^{++}]$. These results were duplicated with 0.8*N* $HClO_4$. In the case of HNO_3, this relation no longer held because of the effect of radiation on the NO_3^- ion. C. H. F.

3

1

Oxidation of organic compounds by molecular oxygen under the action of ionizing radiations. I. Formation of peroxide compounds in liquid hydrocarbons. N. A. Bakh. *Sbornik Rabot Radiatsionnoi Khim.* Akad. Nauk S.S.S.R. 1955, 145-52. X [illegible] liquid [illegible] with O_2 was [illegible] ROOH and H_2O_2 [illegible] heptane, isooctane [illegible] MeC [illegible] cyclohexane yields [illegible] of ROOH while C_6H_6 yields [illegible] ROOH and H_2O_2 [illegible] peroxide [illegible] exceed 1.2 mols per [illegible] and the process is apparently a typical radical reaction. **II. Formation of stable products of oxidation in hydrocarbons of various structures.** N. A. Bakh and N. I. Popov. *Ibid.* 156-62. X-radiation and electron beams cause the mixts. of hydrocarbons with O_2 to form carbonyl compds. in the following yields (mols per 100 e.v.): heptane 2, isooctane 1.2, cyclohexane [illegible] as well as acids in yields of 0.4, 0.6, and 1.2, resp. [illegible] yields PhOH (0.6) and an aldehyde (0.45) but no acids. Radiation yield is independent of temp. and dosage. **III. Oxidative radiolysis of ethyl alcohol.** N. A. Bakh and Yu. I. Sorokin. *Ibid.* 163-74.—X-irradiation or electron bombardment of EtOH in the absence of O_2 yields AcH, H_2O, H_2, CH_4, and CO, with summary yield of [illegible] per 100 e.v. In the presence of dissolved O_2 the yield of these products [illegible] higher [illegible] acids [illegible] magnitude [illegible] the summary [illegible] process is apparently a [illegible] form the aldehyde and ketone [illegible] radical reactions occur with capture [illegible]. **IV. Oxidative radiolysis of** acetic acid. N. A. Bakh and V. V. Saraeva. *Ibid.* 175-[illegible]. The following products and yields were obtained with O_2 in the absence [illegible] resp. yields in mols per 100 e.v. [illegible] irradiation of AcOH, H_2O_2 and AcOOH [illegible] MeCOOH 0.85, 1.1 [illegible] Me_2CO 0.45, 0.45, 0.45, CO_2 2.4, 2.4, CH_4 [illegible] 2.4, total gas 2.4, [illegible] 5.4. The probable sources of the products are discussed. G. M. Kosolapoff.

③

BAKH, N.A.

PHASE I BOOK EXPLOITATION SOV/1140

21(8) (p 4

Vsesoyuznoye soveshchaniye po radiatsionnoy khimii. 1st, Moscow, 1957.

Trudy (Transactions of the First Conference on Radiation Chemistry) Moscow, Izd-vo AN SSSR, 1958. 330 p. 4,000 copies printed.

Sponsoring Agencies: Akademiya nauk SSSR. Otdeleniye khimicheskikh nauk, and U.S.S.R. Ministerstvo khimicheskoy promyshlennosti.

Editorial Board: Bakh, N.A. Professor (resp. ed.); Medvedev, S.S., Corresponding Member, Academy of Sciences, USSR; Veselovskiy, V.I., Professor, Dolin, P.I., Doctor of Chemical Sciences; Miller, N.B., Candidate of Chemical Sciences; Tsetlin, B.L., Candidate of Chemical Sciences (Secretary). Eds. of Publishing House: Trifonov, D.N. and Bugayenko, L.T.; Tech. Ed.: Moskvicheva, N.I.

PURPOSE: This book publishes the reports of the First All-Union Conference on Radiation Chemistry in Moscow, March 25 - 30.

COVERAGE: This collection includes fifty-seven reports and follow-up discussions of each sub-group of reports classified as follows:

Card 1/15

1) primary functions in radiation-chemical processes,
2) radiation chemistry of water solutions (inorganic and organic systems),
3) radiation-electrochemical processes,
4) the effect of radiation on substances which take part in biochemical processes,
5) radiation chemistry of simple organic systems,
6) radiation effects on polymers, and
7) sources of radiation.

According to the editors, the discussions reveal differences in points of view of Soviet scientists on various problems of radiation chemistry; specifically, the mechanism of the action of radiation on concentrated water solutions, the practical importance of radiation-galvanic phenomena, the mechanism of the action of radiation on polymers, etc. The editors also note that the conference revealed inadequate development in some important areas of radiation chemistry, particularly the theory of initiation of radiolysis, and the action of radiation on solid bodies.

SOV/1140

Transactions of the First (Cont.)

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PART I. PRIMARY FUNCTIONS IN RADIATION-CHEMICAL PROCESSES

PART II. RADIATION CHEMISTRY OF WATER SOLUTIONS (INORGANIC AND ORGANIC SYSTEMS)

BAKH, N. A.

PHASE I BOOK EXPLOITATION 978

Vsesoyuznaya nauchno-tekhnicheskaya konferentsiya po primeneniyu radioaktivnykh i stabel'nykh izotopov i izlucheniy v narodnom khozyaystve i nauke. 2d, Moscow, 1957.

Izotopy i izlucheniya v khimii; [sbornik dokladov...] (Isotopes and Radiation in Chemistry; Collection of Papers of the Second All-Union Scientific Technical Conference on the Use of Radioactive and Stable Isotopes and Radiation in the National Economy and Science) Moscow, Izd-vo AN SSSR, 1958. 380 p. 5,000 copies printed.

Sponsoring Agencies: Akademiya nauk SSSR, and SSSR Glavnoye upravleniye po ispol'zovaniyu atomnoy energii.

Editorial Board: Vinogradov, A.P., Academician (Resp. Ed.), Kondrat'yev, V.N., Academician, Alimarin, I.P., Corresponding Member, USSR Academy of Sciences, Bakh, N.A., Dr. of Chemical Sciences, Nikolayev, A.V., Dr. of Chemical Sciences, Nekrasova, G.A., Candidate of Technical Sciences (Secretary); Tech. Ed.: Makuni, Ye.V.

PURPOSE: This book is intended for scientists and technicians engaged in research

Card 1/13

which involves the use of radioactive isotopes or the chemistry of radioactive substances.

COVERAGE: This volume publishes the reports of the Chemistry Section of the Second All-Union Scientific and Technical Conference on the Use of Radioactive and Stable Isotopes and Radiation in Science and the National Economy, sponsored by the Academy of Sciences of the USSR and the Main Administration for the Utilization of Atomic Energy under the Council of Ministers of the USSR. The conference was held in Moscow on April 4-12, 1957. Over fifty reports are included, mainly on radiochemistry, radiation chemistry, methods of obtaining tagged compounds and the use of isotopes in the study of the kinetics and mechanism of chemical reactions in analytical chemistry, physicochemical analysis, etc.

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PART I. KINETICS AND MECHANISM OF CHEMICAL REACTIONS

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Isotopes and Radiation in Chemistry (Cont.) 978

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PART II. RADIATION CHEMISTRY

Isotopes and Radiation in Chemistry (Cont.) 978

PART III. ANALYTICAL CHEMISTRY AND PHYSICOCHEMICAL ANALYSIS

Card 6/13

BAKH, N. A.

"Radiolysis and Radiation Oxidation of Organic Compounds."

paper to be presented at 2nd UN Intl. Conf. on the peaceful uses of Atomic, Energy, Geneva, 1 - 13 Sep 58.

BAKH, N. A.

"Oxygen and Peroxide Effects in Organic Liquids"
paper presented at
session on Role of Oxygen and Perodides in Radiation Chemistry, Intl. Congress on Radiation Research, 10-16 Agu 1958, Burlington Vermont.

KUZIN, A.M.; BAKH, N.A.; MEYSEL', M.N.; POBEDINSKIY, M.N.; PETROV, V.A.

Work at the International Congress on Radiological Research.
Biofizika 3 no.6:746-754 '58. (MIRA 12:1)
(BURLINGTON, VT.--RADIOLOGY--CONGRESSES)

BAKH, N. A.

89-2-7/35

AUTHORS: Popov, M. I., Medvedovskiy, V. I., Bakh, N. A.

TITLE: The Effect of Irradiation on the Valence State of Nitrates-of-Plutonium-Solutions (Vliyaniye izlucheniya na valentnoye sostoyaniye plutoniya v azotnokislykh rastvorakh).

PERIODICAL: Atomnaya Energiya, 1958 Nr 2, pp. 154-160 (USSR).

ABSTRACT:

The investigations were conducted with 0,3 to 2,0 molar nitrates-of-plutonium solution as well as with 0,3 molar nitric acid, which contained different concentrations of $UO_2(NO_3)_2$ and $K_2Cr_2O_7$.

An X-ray tube (5o kV, 2oo mA) was employed as radiation source. The temperature of the liquids was controlled by a thermocouple. The dosimetric quantity, which was used to irradiate the liquids, was determined with the help of a ferrous sulfate-dosimetric method. The doses used were between 5.10^{16} to 7.10^{16} eV/cm^3.sec. The valence states of Pu were determined from the common pairs of

$PuO_2^{+} + PuO_2^{++}$ and $Pu^{+3} + Pu^{+4}$.

An irradiation of nitrates-of-plutonium-solutions, which contain no $UO_2(NO_3)_2$, causes only an oxidation of plutonium. The intensity of the oxidation decreases with an increasing concentration of the NO_3^-

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The Effect of Irradiation on the Valence State of Nitrates-of-Plutonium-Solutions. 89-2-7/35

ions and of the acidity. The assumption is pronounced, that the oxidation is caused by the OH - radicals. In the presence of $UO_2(NO_3)_2$ a reduction of plutonium occurs on certain conditions, which is caused apparently not by the atomic hydrogen, but by the UO_2-ions. An addition of potassium bichromate has an accelerating effect on the radiation oxidation of plutonium. On certain experimental conditions, however, an addition of $K_2Cr_2O_7$ does not prevent the reduction of plutonium.

There are 7 figures, and 15 references, 4 of which are Slavic.

SUBMITTED: April 23, 1957.

AVAILABLE: Library of Congress.

Card 2/2 **1. Plutonium nitrates-Effect of irradiation 2. Radiation-Chemical effects**

SOV/30-58-10-3/53

AUTHORS: Bakh, N. A., Dolin, P. I., Doctors of Chemical Sciences

TITLE: Radiation Chemistry, Its Basic Methods and Tasks (Radiatsionnaya khimiya, yeye osnovnyye napravleniya i zadachi)

PERIODICAL: Vestnik Akademii nauk SSSR, 1958, Nr 10, pp 20-33 (USSR)

ABSTRACT: The authors give the most important methods of modern radiation chemistry, examine their stages of development and discuss their future tasks:

Transfer of the radiation energy on the surroundings, elementary acts of radiation and primary chemical processes.

The transfer of radiation energy upon the surrounding molecules depends on the **laws governing** the interaction between radiation and the material. The theory of energy transfer has only been developed for gases. For the clarification of the process of chemical reaction under radiation, methods of mass spectrometry, of para-magnetic resonance, of spectrometry and others are employed. In the Soviet Union V. L. Tal'roze, N. I. Tunitskiy, and V. V. Voyevodskiy work in this field (Ref 4).

Chemical reactions under radiation of simple inorganic substances.

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These reactions can be most easily explained with examples as the ozone formation, nitrogen oxidation, formation and decomposition of hydrogen peroxide and others. S. Ya. Pshezhetskiy works on this in the USSR (Ref 5).
Chemical reactions under radiation in water and aqueous solutions.
Many papers deal with this problem, as water is being used as moderator and cooling agent in atomic reactors. M. A. Proskurnin and his collaborators are concerned with this problem (Ref 8).
Electro-chemical processes under radiation.
V. I. Veselovskiy (Ref 9) discovered that the irradiation of an electro-chemical system leads to an interference with the thermodynamic equilibrium in that system. In their studies N. A. Bakh and V. I. Medvedovskiy (Ref 10) established the usefulness of electro-chemical methods for the examination of radiolysis products in aqueous solutions.
Research in the field of radiation chemistry of organic compounds.
Because of the complexity, no final results have been achieved. Valuable results were obtained by V. L. Tal'roze, Ye. P.
Card 2/5 Frankevich (Ref 11), A. V. Topchiyev, and L. S. Polyak.

Radiation Chemistry, Its Basic Methods and Tasks SOV/30-58-10-3/53

Radiation polymerization and chemical transformation of polymers under radiation.

In the USSR S. S. Medvedev (Ref 13) carried out systematic research on radiation polymerization. Radiation effects on polymer materials were dealt with by V. A. Kargin and P. A. Rebinder (Ref 14) and are presently studied by V. L. Karpov, B. L. Tsetlin, Yu. S. Lazurkin, and others (Ref 15). The practical application of the chemical transformation of polymers under radiation is only about to be realized.

Radiation effects on solid substances.

There are only very few such studies in the USSR and abroad.

There are 15 references, 13 of which are Soviet.

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76-32-2-1/38

AUTHORS: Bakh, N. A., Sarayeva, V. V.

TITLE: Oxidation Processes in Organic Systems Under the Influence of Ionizing Radiation (Okislitel'nyye protsessy v organicheskikh sistemakh pod deystviyem ioniziruyushchikh izlucheniy)

PERIODICAL: Zhurnal Fizicheskoy Khimii, 1958, Vol. 32, Nr 2, pp. 209-216 (USSR)

ABSTRACT: Primarily, the following process is investigated here: the radiation oxidation of the individual compounds at the expense of molecular oxygen and on such conditions where the radiation energy is directly absorbed by the oxidizing molecules, the molecules being put into a reactive state because of ionization, excitation and the decomposition of radicals. - The formulation of the problem includes the explanation of the nature and the yield of the products forming in the reaction in dependence on the parameters which characterize the radiation (ionization density), the irradiated substances (molecular structure, state of aggregation) and the conditions of irradiation (quantity of dosage, temperature

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Oxidation Processes in Organic Systems Under the Influence of Ionizing Radiation

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etc.). The present work is based on the experimental results of the last years obtained by the scientific collectives of the Laboratories for Radiation Chemistry at the Institute for Physical Chemistry of the AS USSR as well as at the Moscow State University. The here developed ideas on the mechanism of radiation oxidation can be summarized as follows: The oxidation of organic compounds by radiation differs from photochemical and non-catalytic thermal oxidation by the fact that it is in the position to take place with a definite yield. This is the case on conditions where the development of the chain processes does not take place with a measurable velocity, and the oxidation products in it are not consecutively formed but are formed simultaneously. These characteristic features can be explained when it is assumed that the primary radicals R and the peroxide radicals RO_2 forming from them have an excess energy which is sufficient for the isomerization as well as for the interaction with not excited molecules at room temperature or at a lower temperature, - while the secondary radicals forming in it are not capable of repeating these reactions. The results of the present investigations of the interaction processes between ions and molecules show that the energy

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Oxidation Processes in Organic Systems Under the Influence of Ionizing Radiation

76-32-2-1/38

necessary for the excitation of the radicals can be secured by the primary acts of radiolysis. There are 4 figures, 2 tables, and 28 references, 19 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR, Institut fizicheskoy khimii i Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova (Institute for Physical Chemistry, AS USSR, and Moscow State University imeni M. V. Lomonosov)

SUBMITTED: November 1, 1957

1. Organic compounds--Oxidation 2. Organic compounds--Effects of radiation

Card 3/3

PHASE I BOOK EXPLOITATION SOV/3064

International Conference on the Peaceful Uses of Atomic Energy. 2d, Geneva, 1958.

Doklady sovetskikh uchenykh. [t.4] Khimiya radioelementov i radiatsionnykh prevrashcheniy (Reports of Soviet Scientists. v. 4.: Chemistry of Radio- elements and Radiation Transformations) Moscow, Atomizdat, 1959. 323 p. 8,000 copies printed. (Series: Its: Trudy)

Ed. (Title page): A. P. Vinogradov, Academician; Ed.: V. I. Labaznov; Tech. Ed.: Ye. I. Mazel'.

PURPOSE: This collection of articles is intended for scientists and engineers interested in the applications of radioactive materials in science and industry.

COVERAGE: The book contains 26 separate studies concerning various aspects of the chemistry of certain radioactive elements and the processes of radiation effect on matter. These reports discuss present-day methods of reprocessing irradiated nuclear fuel, research in the chemistry of mercury, thorium, uranium, plutonium, and americium, problems related to the sorption and bury- ing of radioactive wastes, the radiolysis of aqueous solutions and of organic compounds, the mechanism of polymer chain grafting, and the effect of radiation on natural and synthetic rubbers. V. N. Prusakov edited the present volume. Most of the reports are accompanied by references. Con- tributors to individual investigations are mentioned in annotations to the Table of Contents.

TABLE OF CONTENTS:

(31)

31959
S/081/61/000/023/007/061
B108/B147

5 4600

AUTHOR: Bakh, N. A.

TITLE: Formation of organic peroxides under the action of radiation

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 23, 1961, 62, abstract 23B462 (Sb. "Rol' perekisey i kisloroda v nach. stadiyakh radiobiol. effekta". M., AN SSSR, 1960, 9 - 19)

TEXT: The formation of peroxides in *n*-heptane, *n*-nonane, and isopropyl ether under the action of X rays has been studied. The yield in peroxides changes only little with temperature between -80 and +80°C in the case of *n*-heptane, and between -50 and + 10°C in the case of isopropyl ether. However, if temperature is raised to 80 - 130°C, the yield will increase considerably and reach about 36.0 for *n*-heptane and 200.0 for isopropyl ether. The activation energies are 16.0 and 13.5 kcal/mole, respectively. The high yields in the temperature-dependent range is explained by the course of chain reactions. [Abstracter's note: Complete translation.]

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86408
S/062/60/000/008/016/033/XX
B013/B055

26.2521

AUTHORS: Bakh, N. A. and Bityukov, V. D.

TITLE: Potentials of Pt- and Au Electrodes in HNO_3 and $NaNO_3$ Solutions Under the Influence of Ionizing Radiation

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1960, No. 8, pp. 1358-1368

TEXT: Changes in the potentials of platinum and gold electrodes in nitric acid- and sodium nitrate solutions under the influence of X-rays were studied. A БФВ-70 (BFV-70) X-ray tube operating at 50 kv and 20 - 200 ma was used as radiation source. Irradiation of the solution and potential measurement were carried out according to the method described in Ref. 1. The solutions were prepared with bidistilled water which had been treated with $KMnO_4$. The platinum electrode was treated with boiling nitric acid, washed with water and then immersed in the solution until it had reached the potential characteristic of the solution in question. The Au electrode was treated with boiling hydrochloric acid and then treated in the same way as the Pt electrode. It was found that the reactions at Pt and Au

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Potentials of Pt- and Au Electrodes in HNO_3 and $NaNO_3$ Solutions Under the Influence of Ionizing Radiation

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electrodes which are determinative for their potentials in nitrate solutions depend on the nature and configuration of the products formed under the influence of radiation. The change in potential observed during irradiation is connected with the fact that, owing to a change in the composition of the solution, individual electrode reactions compete with each other. The electrode potential during irradiation was found to differ from that after irradiation had been stopped. This indicates that short-lived intermediate- or gaseous products of radiation processes whose concentration changes after irradiation has been stopped, are involved in the electrode reactions. The following features are characteristic of the course of the potential change during irradiation: A marked shift in positive direction at the outset of irradiation. The Au electrode retains a high positive potential on increasing the irradiation dose. At a corresponding ratio of irradiation dose and concentration, the potential of the Pt electrode is shifted in negative direction. The total course of the Pt electrode potential can be explained qualitatively by the following sequence of electrode reactions: The positive shift at the outset of irradiation is caused by the highest oxides (probably NO_3) formed in the

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Potentials of Pt- and Au Electrodes in HNO_3 and $NaNO_3$ Solutions Under the Influence of Ionizing Radiation

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solution in yields of the same order of magnitude as the yield of OH radicals ($G \geqslant 3$). The molecular hydrogen $[G (H_2 \leqslant 0.5)]$ formed simultaneously with a yield lower by one order of magnitude quickly reaches a stationary concentration. The latter may be sufficient ($\sim 10^{-6}$ M) or insufficient ($\sim 10^{-8}$ M) to produce a potential shift in negative direction. In the most favorable case, it approaches the hydrogen potential. In acid solutions, the third product formed simultaneously is HNO_2. During the accumulation of HNO_2 the potential shifts in positive direction, reaching a stationary value at $3 - 5 \cdot 10^{19}$ ev/cm^3. An additional potential shift after irradiation has been stopped probably corresponds to the final separation of gaseous products. In conclusion it may be said that both the reaction products of the radiation-induced transformation of nitrate ions and, in the case of the platinum electrode, the product of primary radiolysis, molecular hydrogen, are involved in the stabilization of the potential. V. I. Veselovskiy is mentioned. There are 9 figures and 14 references: 9 Soviet, 3 German, 1 British, and 1 US.

ASSOCIATION: Institut elektrokhimii Akademii nauk SSSR (Institute of Electrochemistry of the Academy of Sciences USSR)

SUBMITTED: January 29, 1959

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81571

S/076/60/034/06/14/040
B015/B061

5.4500(B)

AUTHORS: Bugayenko, L. T., Kalyazin, Ye. P., Bakh, N. A. (Moscow)

TITLE: Radiochemistry of Oxychloride Compounds. I. The Action of X Rays on Aqueous Sodium Chlorite Solutions

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol. 34, No. 6, pp. 1243-1249

TEXT: The conversion of the ClO_2^- ion in neutral aqueous 0.001 M $NaClO_2$-solutions by the action of 65-kv X rays was examined. A Roentgen tube of the type TPЦ-3A (TRTs-3A) was used as radiation source, and chlorite, chlorine dioxide, and hydrogen peroxide were determined with an СФ-4 (SF-4) spectrophotometer, whilst chloride, hypochlorite, and chlorate were determined with an ФЭК-1 (FEK-1) photoelectrocolorimeter. The tests were carried out on $NaClO_2$-solutions saturated with hydrogen, nitrogen, and oxygen. The conversion products obtained with a radiation dose of $5\cdot10^{18}$ ev/ml are tabulated. It was established that an oxidation

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Radiochemistry of Oxychloride Compounds.
I. The Action of X Rays on Aqueous
Sodium Chlorite Solutions

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of the chlorite ion to chlorine dioxide and to the chlorate ion takes place, and a reduction to hypochlorite- and chloride ions, when the hypochlorite ion and chlorine dioxide occur as intermediate products. Hydrogen peroxide forms only when all hypochlorite ions are decomposed. In solutions saturated with oxygen, the yield of oxidation and reduction products is much smaller, and no hypochlorite ion occurs, on the other hand hydrogen peroxide forms from the very beginning of the radiation action. Based on the results, a reaction mechanism for the conversion of the chlorite ions in aqueous solutions by the effect of radiation is proposed. There are 4 figures, 1 table, and 21 references: 6 Soviet, 7 American, 1 Canadian, 1 Hungarian, 1 German, and 1 Swiss.

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

SUBMITTED: August 2, 1958

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Card 2/2

BAKH, N.A.; BABICHEVA, G.G.; LARIN, V.A.

Radiation oxidation of leuco bases in ketones in the absence of oxygen. Dokl. AN SSSR 134 no.5:1079-1082 O '60. (MIRA 13:10)

1. Institut elektrokhimii Akademii nauk SSSR. Predstavleno akademikom A.N.Frumkinym.
(Dyes and dyeing) (Oxidation)

23773

5.3830 1209 1234 1372

S/190/61/003/006/016/019
B110/B208

AUTHORS: Pshezhetskiy, V. S., Kargin, V. A., Bakh, N. A.

TITLE: Polymerization of acetaldehyde in the condensed phase under the action of X-rays

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 6, 1961, 925 - 930

TEXT: According to M. Naga et al. (Ref. 1: Simpozium po makromolekulyarnoy khimii, Moskva, June, 1960. Khimiya i tekhnologiya polimerov, No. 7 - 8, 102, 1960) polymerization in the solid phase takes place at low temperatures under the action of ionizing radiation. V. A. Kargin, V. A. Kabanov and V. P. Zubov (Ref. 8: Vysokomolek. soyed., 265, 1959) observed a transition from the amorphous into the crystalline state in the polymerization. According to N. N. Semenov (Ref. 9: Simpozium po makromolekulyarnoy khimii, Moskva, June, 1960. Khimiya i tekhnologiya polimerov, No. 7 - 8, 196, 1960) the crystal lattice causes a special polymerization mechanism. The authors studied the acetaldehyde polymerization by means of X-rays in the solid phase. The acetaldehyde fraction (boiling

X

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point 20.1 - 20.4°C/760 mm and n_D^6 = 1.34[illegible]) was allowed to solidify in 10-ml ampuls filled with N_2 (residual pressure 10^{-4} mm) for 30 sec. The sample was irradiated with the ВХВ (VKhV) X-ray tube with ~ 60 kv and 100 ma at the temperature of liquid nitrogen as well as at different temperatures in the cryostat. The absorption energy was determined on the ferrous sulfate dosimeter. The polymerizate was dissolved in acetone with 1 % inhibitor (naphthylamine), precipitated in water; the molecular weights were determined viscosimetrically in methyl ethyl ketone at 17.8°C according to: $[\eta] = 5.36\cdot 10^{-4}M^{0.65}$. The absence of the increase of the conversion degree (Fig. 1) as well as the decrease of molecular weight with increasing integral radiation dose are indicative of destruction processes in addition to polymerization. In order to explain the influence of the physical conditions of the phase upon the polymerization the monomer was cooled down under different conditions. Quick cooling for 1 min gave a transparent amorphous monomer. Slow cooling of the liquid and cooling of the vapors gave monomers with different degrees of crystallinity. Irradiation was made at different temperatures. As, according to Table 2, the degree of monomer conversion and the polymer

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B110/B208

Polymerization of acetaldehyde. .

molecular weight are directly proportional to the degree of crystallinity, acetaldehyde is polymerized by X-rays in the crystalline phase. Polymerization takes place according to G. Moravtsev (Ref. 4: Khimiya i tekhnologiya polimerov, No. 10, 23, 1959) as radical mechanism polymerization (I), similarly as in the liquid phase or by radical migration in the crystal lattice (II) or according to N. N. Semenov (Ref. 9: Simpozium po makromolekulyarnoy khimii, Moskva, June, 1960. Khimiya i tekhnologiya polimerov, No. 7 - 8, 196, 1960). In the case of (I) the radical acceptors are said to have a negative effect on polymerization, and a difference should exist between these and substances with similar configuration, which, however, do not accept radicals. In (II), this difference is not assumed to exist. The authors determined yield and molecular weight on incorporation of various admixtures into acetaldehyde. All admixtures having nearly the same effect on the degree of conversion, this must be due to fracture of the crystal lattice. The latter had to be the greater, the larger the geometric molecular dimensions are. The effect observed is due to the formation of some defect in the crystal lattice. Polymerization thus takes place in the solid phase, otherwise the effect of the admixtures would not be so homogeneous and intense.

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B110/B208

Polymerization of acetaldehyde..

The results obtained indicate a polymerization in the solid phase due to properties of the crystal lattice. The number of the ion pairs formed may be estimated from the absorbed radiant energy, and compared with the number of molecular chains calculated from the molecular weights. If the formation of an ion pair gives rise to the formation of a reaction chain, the ionizing energy absorbed will be 30 ev. At a total absorbed energy of 10^{19} ev/cm^3, $3.3\cdot10^{17}$ reaction chains appear per cm^3. For $\bar{M} = 600,000$; $P_n = 13,300$, conversion degree 35.2 %; initial monomer = 7.8 g the total number of molecules per cm^3 was: $n = 3.66\cdot10^{21}$, and the mean number of molecular chains: $n/P = 2.7\cdot10^{17}$. The latter corresponds to the number of ion pairs. A reaction chain is thus formed during the formation of each ion pair. The authors conclude from their thermodynamic data and thermographic measurements that this polymerization mechanism is no radical mechanism. Temperature change from -195°C to -132°C does not affect the reaction rate. Slight increase of the conversion degree is due to increasing molecule mobility. When, however, the melting point is passed, the conversion degree decreases abruptly. The activation energy is 0.45 kcal/mole. The authors conclude from all results that the polymeri-

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23773

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B110/B208

Polymerization of acetaldehyde...

zation of acetaldehyde in the solid phase takes place by means of expansion on the crystal lattice.
There are 2 figures, 4 tables, and 11 references: 4 Soviet-bloc and 7 non-Soviet-bloc. The three most recent references to English-language publications read as follows: E. J. Lawton; W. T. Grubb; J. S. Balwit, J. Polymer Sci., 19, 455, 1956. Ref. 6: G. Adler: J. Chem. Phys., 31, 848, 1959. Ref. 7: B. Baysal, G. Adler, D. Ballantine, P. Colombo. J. Polymer Sci., 44, 117, 1960.

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

SUBMITTED: November 4, 1960

Card 5/8

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5.4600 2209 1304

25785
S/020/61/139/002/0[illegible]/017
B103/B220

AUTHORS: Larin, V. A., and Bakh, N. A.

TITLE: Oxidation and reduction of organic compounds by radical products of radiolysis

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 139, no. 2, 1961, 406-409

TEXT: The authors continue their studies of oxidation and reduction of organic dyes by radiolytic products of organic solvents (N. A. Bakh et al., Ref. 1: DAN, 134, 1079 (1960); A. I. Chernova et al., Ref. 2: ZhFKh, 30, 1343 (1956)). They made again use of the reversible redox pair methylene blue (MB) - Leucobasis (LMB) as indicator of the redox processes. It is proved that - dependent on the nature of the organic solvent - radiation may effect oxidation of LMB as well as reduction of MB. Solutions of LMB and MB (10^{-6}-10^{-4} M) in (1) acetone, (2) nitro methane, (3) methanol, (4) ethanol, (5) n propanol, (6) n-butanol, (7) formamide, (8) pyridine, (9) N methyl formamide, and (10) N,N-dimethyl formamide were irradiated with X rays and gamma rays (intensity of dose $2.8 \cdot 10^{12}$ to $5 \cdot 10^{17}$ ev/cm^3 per sec). Th

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Oxidation and reduction of organic ...

solvents were purified carefully. MB was recrystallized repeatedly from water and from ethanol. The colorless solutions of LMB were prepared by reducing MB by hydrogen in the presence of platinum black and the absence of air. The solutions were sealed in ampules in nitrogen atmosphere and irradiated and spectrophotometered in these ampules. MB is reduced reversibly to LMB under these conditions in all solvents (1)-(10). (A) Reduction of LMB. In (1), (2) and (3), the colorless solutions of LMB become colored. Comparison of the absorption spectra shows that LMB is oxidized to MB on irradiation. Fig. 1 shows the yield in radiative oxidation of LMB to MB as function of the concentration. (B) Reduction of MB: The solutions of MB saturated with nitrogen of (1)-(10) are decolorized with more or less yield on irradiation, the decolorization is, however, not in all cases due to the reduction of MB to LMB. The criterion of this reduction is the complete reestablishment of the initial color intensity on introduction of oxygen into the solution. The curves of Fig. 2 correspond to irradiation in nitrogen atmosphere and to conservation without irradiation after the introduction of oxygen. They show 3 possible cases: (a) a completely reversible reduction to LMG in (7); (b) a partial reduction to LMB and an irreversible decolorization in (9), and (c) a completely

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irreversible decolorization in (10). The slope of the linear initial sections of the curves corresponds to the radiative yield of the reaction and is dependent on the initial concentration of the dye. Fig. 3 represents the yield of the reversible reduction as function of the concentration of MB in several solvents. The function is analogous to that in case (A). Figs. 1 and 3 show the effect of functional groups in the molecules of organic solvents on reactions (A) and (B): in (2), mere oxidation of LMB is effected, in (3) oxidation of LMB is accompanied by simultaneous reduction of MB, whereas in aliphatic normal alcohols (from ethanol onwards) in (7) and (8) merely a reversible reduction of MB to LMB occurs. The direct radiative effect up to concentrations of ~ 10^{-2} M on the substance dissolved is neglected, since here all processes are determined by the interaction between the acceptor and the radiolytic products of the solvent. Although the molecular products (HNO_2, HCHO, CH_3CHO, etc.) which are formed by radiation act sometimes on the acceptors as oxidizers or reducing agents, their effect during radiation was negligible and the processes take place merely due to the effect of the short-lived radiolytic products. The horizontal part of the curves in Figs. 1 and 3 in the concentration range of ~ 10^{-4} to 10^{-2} M corresponds to a complete capture

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of the radicals susceptible to this reaction by the acceptor. The further increase of the yield corresponds to a new process. The authors tend to the hypothesis that oxidation as well as reduction are effected in diluted solutions (in organic solvents) by the primary radicals of the radiolytic products of the solvent. Direction and efficiency of the process depend on the nature of the radicals and their yield. The redox pair MB - LMB corresponds to a two-stage transition. The authors suggest that in the said system merely a one-stage transition from LMB or MB to the intermediary semiquinone is effected by primary radicals. The final products, however, are formed due to disproportioning according to scheme.
$A \rightsquigarrow \dot{R}$, $\dot{R} + (L \text{ or } M) \longrightarrow \dot{S}$ or $2\dot{S} \longrightarrow M + L$, where A is the solvent, $\dot{S}$ semiquinone, M dye, and L the leucoform as in the non-radiation oxidation and reduction reactions of this type. The authors estimate the yield in primary radicals showing oxidizing or reducing effect on MB and LMB, based on the yields of MB and LMB formation in the range of independence of the concentration of the acceptor.

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B103/B220

Oxidation and reduction of organic ...

Table 1

Solvent	$G_{(\dot{R}_{ox})}$	$G_{(\dot{R}_{red})}$	Solvent	$G_{(\dot{R}_{ox})}$	$G_{(\dot{R}_{red})}$
2	4.0 ± 0.3	0	6	0	4.4 ± 0.2
3	3.6 ± 0.2	2.8 ± 0.2	7	0	6.0 ± 0.4
4	0	7.0 ± 0.2	9	0	4.8 ± 0.2
5	0	6.4 ± 0.4	8	0	1.2 ± 0.2

For (1), the radical oxidation mechanism is improbable. A reaction by partly stimulated acetone molecules is possible, further investigations are, necessary, however. In all cases, the yields remain within limits which may be expected for radicals based on ionization. The functions exerted by the radicals on the acceptors may vary with the latter (methanol). The study of the reactions between free radicals and various acceptors is a source of knowledge with regard to their tendency to absorb or emit electrons under various conditions. For this purpose the radicals effective in the individual case have to be identified. This may be achieved by comparing the conclusions drawn from kinetic studies with those

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Oxidation and reduction of organic ...

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B103/B220

regarding electron paramagnetic resonance. There are 3 figures, 1 table, and 6 references: 2 Soviet-bloc and 4 non-Soviet-bloc. The three references to English language publications read as follows: E. Hayon et al. (Ref. 3: J. Chem. Soc., 1957, 30'). M. J. Day, G. Stein (Ref. 4: Radiation Res., 6, 666 (1957)); L. Michaelis (Ref. 5: Ann. N. Y. Ac. Sci., 40 (2), 399 (1940)).

ASSOCIATION: Institut elektrokhimii Akademii nauk SSSR (Institute of Electrochemistry, Academy of Sciences USSR)

PRESENTED: March 10, 1961 by A. N. Frumkin, Academician

SUBMITTED: March 10, 1961

Card 6/8

30708

54300 1273 2209

S/020/61/141/002/022/027
B101/B110

AUTHORS: Revina, A. A., and Bakh, N. A.

TITLE: Electron paramagnetic resonance study of the interaction of molecular oxygen with a stable free radical in solution

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 141, no. 2, 1961, 409-412

TEXT: It was the object of the authors to pursue the primary reaction of O_2 with radicals. α,α'-diphenyl-β-picryl hydrazyl (I) in benzene solution was used as free radical. This compound was synthesized by A. Ye. Arbuzov and F. G. Valitova by their method (ZhOKh, 27, 2354 (1957)). The investigation was carried out with an ЭПР-2 (EPR-2) spectrometer of IKhF, with 0.08 cm^3 of I being used. The known five epr lines with a width of ~50 oe (number of paramagnetic centers $4 \cdot 10^{16}$) were obtained in vacuo. At p_{O_2} = 150 mm Hg, the spectrum widened to 60 oe, and the number of paramagnetic centers dropped to $3.4 \cdot 10^{16}$. At p_{O_2} = 760 mm Hg,

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the hyperfine structure vanished. The spectrum now only formed a wave of 72 oe width, and the number of paramagnetic centers was $3.0\cdot10^{16}$. After evacuation the initial five-line spectrum reappeared. The effect of the duration of contact between I and O_2 was examined in an ampoule containing O_2 and I in a ratio of ~ 8. After 90 days no free radicals could be observed any longer in the presence of O_2. After evacuation, however, they reappeared. Samples without O_2 did not show a variation of their content of free radicals during this time. The rate of disappearance of free radicals furthermore depended on the addition of O_2. Fig. 3 shows the results obtained for $V_{gas}/V_{liqu} \sim 8; \sim 50;$ and ~ 100. The variation of the epr spectrum of I in the presence of O_2 is ascribed to the superposition of two effects: 1) mere physical interaction caused by the paramagnetic properties of O_2 molecules. This leads to a widening of the lines, but does not affect the unpaired electrons in the system. 2) Chemical interaction which, due to the formation of a peroxide

Electron paramagnetic resonance...

S/020/61/141/002/022/027
B101/B110

compound, leads to the disappearance of I radicals. It decomposes, however, on evacuation. With a longer contact time between I and O_2, final oxidation products of I are formed. Fig. 3 shows that the reaction slows down when there is little O_2 excess. The formation of the primary peroxide compound is a fast reaction while the subsequent conversion of this compound into final oxidation products proceeds slowly. The O_2 consumption was found to be greater than what would have corresponded to the consumption of I. This is explained by the fact that the solvent contributes to the oxidation process. This contribution can also be proved by the occurrence of phenol groups, the amount of which exceeded the amount of phenol groups contained in I. The authors thank Professor L. A. Blyumenfel'd for advice and discussion. There are 3 figures and 11 references: 5 Soviet and 6 non-Soviet. The four most recent references to English-language publications read as follows: T. Matsugashita, K. Shinohara, J. Chem. Phys., 32, 954 (1960); B. R. Loy, J. Polymer Sci., 44, 341 (1960); J. Deduchi, J. Chem. Phys., 32, 1584 (1960); T. H. Brown, D. H. Anderson, H. S. Gutowsky, J. Chem. Phys., 33, 720 (1960)

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30706

Electron paramagnetic resonance...

S/020/61/141/002/022/027
B101/B110

ASSOCIATION: Institut elektrokhimii Akademii nauk SSSR (Institute of Electrochemistry of the Academy of Sciences USSR)

PRESENTED: June 15, 1961, by A. N. Frumkin, Academician

SUBMITTED: May 13, 1961

Fig. 3. Variation of the disappearance rate of I radicals as a function of the total O_2 content in the sample.

Legend: (1) ratio $V_{gas}/V_{liqu} \sim 8$; (2) ratio ~ 100; (3) ratio ~ 50. Continuous lines: Content of free radicals after evacuation. Broken lines: Content of free radicals in the presence of O_2. (a) days; (b) number of radicals.

Card 4/[illegible]

Бах, Н. А.

SESSION E—5—3: Radiation Chemistry of Organic Compounds II.

(a)

Radiation Induced Oxidation and Reduction of Acceptors in Organic Solutions

N. Bach, V. Larin and M. Roder

3

Oxidation and reduction of solutes by the primary radiolysis products of solvents occurs not only in aqueous solutions but also in organic liquids. It is concluded from the dependence of yield on concentration of the acceptor, and from ESR data, that in a number of solvents such as alcohols, nitromethane, formamide, methylformamide, etc., the reactions are effected just as in aqueous solutions by free radicals. However, in other solvents the experimental data are not consistent with this viewpoint, as shown by the behaviour under irradiation of dilute oxygen-free solutions in acetone of Fe^{III}, Fe^{II}, Cu^{II}, Cu^{I}, Cr^{VI}, Cr^{III}, Mn^{VII}, I$^-$, I$_3^-$ and also methylene blue and its leuco form. The reactions are mostly reductions, but in some instances oxidation is observed. The wide variety of yields, ranging from G = 0.8 to G = 26 equiv. per 100 eV, excludes mechanisms based only on free radicals, and requires an important interaction of the acceptor with non-radical short-lived primary products of the radiolysis of acetone. A kinetic scheme is considered which enables the yield of primary products effecting different reactions to be estimated.

Institute of Electrochemistry, Academy of Sciences, Moscow, USSR

report presented at the 2nd Intl. Congress of Radiation Research,
Harrogate/Yorkshire, Gt. Brit. 5-11 Aug 1962

BAKH, N. A.

[illegible] for the investigation of these radicals by ESR spectroscopy. In this case the sensitivity of the spectrometer is not limited by the frequency fluctuations of the klystron, if special arrangements are employed, but by the noise level of the pre-amplifier.

By use of low noise pre amplifiers (e.g. masers) it is then possible to increase the sensitivity of the spectrometer. The conditions for this are calculated.

An X-band ruby maser developed for this application will be discussed. By optimizing the free parameters a stable gain of 32 db and a voltage-gain bandwidth product of 22 Mc was obtained at a crystal temperature of 90 K.

Max Planck Institute for Biophysics, Frankfurt am Main, Germany

Investigation of Early Stages of Radiation-Induced Oxidation by Electron Spin Resonance

[illegible]

A. Revina and N. Bach

A study of the ESR spectra of α, α' diphenyl β-picryl hydrazyl dissolved in benzene has shown that it forms a non-radical product of the peroxide type with O_2. This product decomposes reversibly with regeneration of free radicals on removal of the O_2. If O_2 is not removed, it eventually transforms into the final oxidation products of the free radical.

A similar ESR investigation of the radicals appearing on γ-irradiation of potassium palmitate and other organic substances shows that they also form non-radical peroxidic compounds with O_2, and that these also decompose reversibly on removal of oxygen. In somewhat different conditions typical peroxy-radicals appear. It is deduced that the formation of such labile non-radical compounds of the substrate radicals with molecular O_2 is an early reaction stage in many oxidation processes.

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow

Dose-Response Relationships in the Yield of Radiation-Induced Free Radicals in Amino Acid

report presented at the 2nd Intl. Congress of Radiation Research, Harrogate/Yorkshire, Gt. Brit. 5-11 Aug 1962

S/844/62/000/000/037/129
D214/D307

AUTHORS: Nam Ch'ang Sung and Bakh, N. A.

TITLE: Radiational transformations in two-phase systems of di-iso-propyl ether-water solutions

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 228-232

TEXT: Nuclear radiation, during the extraction of radioactive isotopes by organic solvents, may lead to changes in the organic compounds and in the valency states of the inorganic ions. The aim of this work is to gather information useful in predicting the behavior of such extraction processes. Radiochemical processes in the system di-iso-propyl ether-H_2O were studied in the presence and absence of O_2, HCl and iron chlorides. By irradiating the two separated phases, Fe^{II} is radio-oxidized in the aqueous phase only in

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Radiational transformations in ... S/844/62/000/000/037/129
D214/D307

the presence of HCl and the yield of Fe^{III} increases with the acidity. High yields of carbonyl compounds during radiolysis of the pure ether and the high yield of carbonyl compounds and peroxides during radio-oxidation of the H_2O solution in ether, shows that the reactions proceed by a chain mechanism. Fe^{III} is reduced in the H_2O phase in the absence of O_2, by the ether radicals formed by the interaction of $\dot{O}H$ with the dissolved ether; Fe^{II} is oxidized under these conditions only if O_2 is present. Irradiation of this system in the form of an emulsion leads to the same products. The yield of peroxide and Fe^{II} in the emulsion is equal to the sum of their yields obtained in the separated phases, only at low doses of radiation. At higher doses, the yields in the emulsion are higher due to the redistribution of products among the phases. All Fe^{II} present in the system 6N HCl-ether-O_2 is, on exposure to radiation, oxidized to Fe^{III} which distributed itself between the phases. On

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Radiational transformations in ... S/844/62/000/000/037/129
D214/D307

substituting O_2 by N_2 and on further exposure, Fe^{III} is (in both phases) reduced to Fe^{II} which passes into the H_2O phase. There are 3 figures and 2 tables.

ASSOCIATION: Moskovskiy gosudarstvennyy universitet im. M. V. Lomonosova, khimicheskiy fakul'tet (Moscow State University im. M. V. Lomonosov, Faculty of Chemistry)

Card 3/3

S/844/62/000/000/058/129
D204/D307

AUTHOR: Bakh, N. A.

TITLE: Radiational oxidation and synthesis of organic compounds

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 339-351

TEXT: A review is presented of the recent results achieved by Soviet and western workers in various reactions brought about under the action of ionizing radiation. The main points considered are: (1) oxidation of liquid hydrocarbons with molecular O_2, where the interaction is largely between O_2 and the radiolysis products of the hydrocarbon; (2) vapor phase hydrocarbon-oxidation reactions; (3) oxidation-reduction processes occurring, in the absence of O_2, between the solute and the radiolysis products of the solvent; (4) halogenation (chiefly chlorination reactions of hydrocarbons); (5) sulfonation reactions of organic compounds (mainly hydrocarbons)

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Radiational oxidation and ... S/844/62/000/000/058/129
D204/D307

with SO_2; (6) irradiation of mixtures of unsaturated and saturated compounds, leading to reactions between the radicals, originating from the saturated compound, and the double bonds. Alkylation, halogenation, sulfurization and introduction of phosphorus or silicon are quoted as possible synthetic reactions in this group; (7) formation of organometallics by the irradiation of the metal and an alkyl halide; (8) radiational synthetic reactions not proceeding by a chain mechanism. Numerous examples are given to illustrate points (1) - (8) and reaction mechanisms are discussed. Further research is recommended on the subject of chain reactions initiated by irradiation, and on non-chain processes in which highly active chemical species are formed. There are 3 figures, 2 tables and 50 references.

ASSOCIATION: Institut elektrokhimii AN SSSR (Institute of Electrochemistry, AS USSR)

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S/844/62/000/000/060/129
D204/D307

AUTHORS: Sarayeva, V. V., Bakh, N. A. and Dakin, V. I.

TITLE: Radiational oxidation and radiolysis of di-*iso*-propyl ether

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 357-361

TEXT: The mechanism of the above reaction was studied under the action of x rays, with a constant dose of 3.5×10^{15} ev/cm^3.sec at -23 to +57°C and with doses of $4.3 \times 10^{14} - 1.4 \times 10^{16}$ ev/cm^3.sec at constant temperature. Up to +10°C the yields G (mols per 100 ev) of peroxides and carbonyl compounds were practically independent of temperature; the yields of all products studied (above - acids and alcohols increased rapidly at >10°C). Above 30°C the yields of acids and alcohols plotted against the dose of irradiation gave rise to S-shaped curves, showing the successive formation of products. Log

$G/\frac{1}{T^{o}K}$ curves showed the existence of 2 mechanisms for the formation of peroxides and carbonyl compounds: a radical-molecular non-chain mechanism in the region where $G \not\sim T$, and a chain mechanism at higher temperatures. The latter was confirmed by experiments carried out at various irradiation doses or in the presence of chain inhibitors. No significant oxidation of the ether was observed even at 50°C in the absence of previous irradiation; after irradiation the reaction proceeded only above 40°C. Decomposition of the peroxide product was demonstrated to be easier under the action of x rays than under the influence of heat. Radiolysis of the ether at 25°C in the absence of oxygen showed that the yields of carbonyl compounds increased with decreasing dose of irradiation, whilst those of alcohols became lower. This and the strong influence of admixtures on the reaction indicates a chain mechanism; the alcohols are believed to form as a result of chain-breaking. There are 5 figures.

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S/844/62/000/000/063/129
D204/D307

AUTHORS: Larin, V. A. and Bakh, N. A.

TITLE: Reactions of oxidation-reduction acceptors with the products of the radiolysis of organic solvents

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 374-377

TEXT: A discussion of earlier work (DAN SSSR, 134, 1074, 1079 (1960)) in which oxidation reactions induced in various solvents by irradiation in the absence of oxygen were followed using the conjugate pair methylene blue-methylene blue leucobase (MB-LMB) as an indicator of dye-radical interactions. With increasing concentration of the acceptor, the radiation yield, G, increased to a constant value (full utilization of available radicals by the dye) and then increased again, showing the existence of a different mechanism. MB solutions are always bleached on irradiation under N_2, the criterion of MB $\longrightarrow$ LMB reduction alone being full recovery of color

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(as e.g. in MeOH), when O_2 is admitted to the system. Some irradiated solutions of MB, particularly in aldehydes and esters, did not regain their color; the graphs of G against log C_{MB} (where C_{MB} = acceptor concentration), plotted for such solvents, showed that G increased with increasing log C_M, up to constant values different for each solvent. The plots of $\frac{1}{G}/\frac{1}{C_{MB}}$ were linear, confirming that these reactions also involve the free-radical radiolysis products of each solvent. The bleaching of MB in acetone was only 85% irreversible. The decolorization is fully irreversible in N-dimethylformamide and reversible in formamide. The mechanism of irreversible destruction of the dye on irradiation is not as yet completely understood and my be different in various types of solvents. There are 5 figures and 1 table.

ASSOCIATION: Institut elektrokhimii AN SSSR (Institute of Electrochemistry AS USSR)

S/844/62/000/000/064/129
D204/D307

AUTHORS: Roder, M., Bakh, N. A. and Bugayenko, L. T.

TITLE: Radiation-chemical transformations of chromium compounds dissolved in acetone

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 378-381

TEXT: The oxidation-reduction transformations of Cr^{III} and Cr^{VI} compounds were studied, in continuation of earlier work (this collection, p. 374) connected with such transformation of methylene blue and its leucobase, under the action of x rays (10^{16} ev/ml.sec) at 16°C. The compounds were dissolved in the form of $CrCl_3.6H_2O$ and CrO_3. After irradiation $Cr^{VI} \longrightarrow Cr^{III}$, with reduction yields G_{red}, (eqts/100 ev) which increased with concentration of CrO_3,c, both in the presence of (1) N_2 and (2) O_2. G_{red} varied between (1)~5 and

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Radiation-chemical transformations... D204/D307

~11 and (2) ~1.5 and ~3, no significant rise being observed when c was increased above 5 x 10^{-3} M; this is similar to the transformations occurring in aqueous solutions. The plateaus in G_{red}/c curves indicate an interaction with the free-radical radiolysis products of acetone. The radiation induced reduction of Cr^{VI} is probably only to Cr^{V}, which immediately disproportionates to the 3- and 6-valent ions. In O_2-saturated solutions $Cr^{III} \rightarrow Cr^{VI}$, with the formation of a Cr^{III} — Cr^{VI} complex; this does not occur in water. The oxidation also involves the free radicals formed when acetone is irradiated. Reduction and oxidation yields are tabulated for various acetone solutions of Cr^{VI}, Cr^{III} and Cr^{III}/Cr^{VI}, showing that G_{red} is appreciably reduced in the presence of Cr^{III}. This is explained by the comparatively high reduction-resistance of the Cr^{III} - Cr^{VI} complex formed. Both transformations occur more effectively in acetone than in water, owing to the higher radical yields in irradiated acetone.

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Radiation-chemical transformation ... S/844/62/000/000/064/129
D204/D307

There are 2 figures and 1 table.

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Card 3/3

S/844/62/000/000/127/129
D444/D307

AUTHORS: Bakh, N. A., Babicheva, G. G. and Larin, V. A.

TITLE: Dose-measuring system for small quantities of absorbed energy

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 738-740

TEXT: The authors' laboratory has previously studied the effect of radiation on the colorless leucobases of triphenylmethane dyes in the presence of molecular oxygen; their disadvantage is a tendency for coloration to be produced by autoxidation with molecular oxygen in the absence of radiation. The high molar coefficient of extinction, however, makes these dyes very suitable for dose measurement and the authors now report a study on the formation of the dye crystal violet by irradiation of its leucobase in acetone and methylethyl ketone in the absence of molecular oxygen. The radiations studied were x rays, γ rays, and alpha particles at tem-

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Dose-measuring system ...

S/844/62/000/000/127/129
D444/D307

peratures from -85 to +50°C. The methylethyl ketone solution is convenient for measuring doses up to about 1500 rads. There are 4 figures.

ASSOCIATION: Institut elektrokhimii AN SSSR (Institute of Electrochemistry, AS USSR)

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S/195/62/003/006/004/011
E075/E436

AUTHORS: Sarayeva, V.V., Bakh, N.A., Dakin, V.I.,
Dillinger, P.

TITLE: Influence of temperature and dose rate on the radiolysis and the radiation induced oxidation of diisopropylether

PERIODICAL: Kinetika i kataliz, v.3, no.6, 1962, 865-869

TEXT: The object of the work was to elucidate the mechanism of decomposition and oxidation of diisopropylether under the action of α and γ irradiation. The ether was freed from peroxides, water and carbonyl compounds and irradiated after evacuation, or in the presence of oxygen, at a range of temperatures (-35 to 70°C). The yield of carbonyl compounds reached a sharp maximum (G = 14.5 mole/100 eV) at about 25°C. At 35°C the yield decreased to about 3 mole/100 eV. Temperature did not affect the formation of alcohols. The carbonyl compounds were formed by chain reaction with an activation energy of 11 kcal/mole, the chain growth being determined by the interaction of isopropyl radicals with the ether molecules. The formation of carbonyl compounds by the chain

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Influence of temperature ... S/195/62/003/006/004/011
E075/E436

reaction was confirmed by the increase of their yield with increasing radiation dosage. No corresponding increase occurred for alcohols, which indicated that they are not formed by chain reaction. In the presence of O_2, the yields of peroxides and carbonyl compounds remain stable at 5.4 and 6.6 mole/100 eV respectively. Above 10°C, the yield increases for all the radiolysis products investigated to about 250 mole/100 eV at 70°C. The values of activation energies for the oxidation above 10°C (15 and 20 kcal for peroxides and carbonyl compounds respectively) indicate that the peroxide results from the reaction of O with an ether molecule, determining the development of a chain reaction, and the carbonyl compounds result from the decomposition of peroxide radicals. For the peroxides $G = kI^{-0.5}$ at 30°C, where I - dose intensity corresponding to the chain process. For carbonyl compounds $G = kI^{-0.7}$, also a chain reaction. Low yields for acids and alcohols indicate that they are not formed by chain reactions, but possibly by isomerization and decomposition of peroxide radicals. These reactions are realized by the excess energy possessed by the radiolysis products at the moment of their
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Influence of temperature ... S/195/62/003/006/004/011
E075/E436

formation. There are 5 figures and 1 table.

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

SUBMITTED: October 25, 1961

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Card 3/3

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S/190/62/004/005/016/026
B110/B108

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AUTHORS: Pshezhetskiy, V. S., Kargin, V. A., Bakh, N. A.

TITLE: Gamma-induced solid-state polymerization of acetaldehyde

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 5, 1962, 728-733

TEXT: A study was made of gamma-induced solid-state polymerization of acetaldehyde single crystals in order to elucidate the role played by the crystal lattice in the process of polymerization. Additions of acetone and methyl cyclohexane may have the following effects: (1) The "host" molecule is inside the crystallite, and hinders the propagation of the polymerization chain in the lattice; (2) the "host" molecule is outside the crystallite, and hinders the propagation of the polymerization chain between the crystallites. It was found that, as in the case of polymerization of acetaldehyde in a polycrystal, small additions to the single crystal lower the degree of conversion (polycrystal, 25%; single crystal, 40%) and the molecular weight ($[\eta]$(polycrystal)-3; $[\eta]$(single crystal)-4). Thus,

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Gamma-induced solid-state ... S/190/62/004/005/016/026
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irrespective of the degree of crystallinity, additives form lattice defects where chain rupture occurs. Thermographic investigation showed that temperature jumps occurred below the melting point of crystalline acetaldehyde when slowly heated at a rate of 1.4°C/min and irradiated with $\sim 10^{19}$ ev/cm^3 at -196°C. As the radiation dose was increased, the jumps shifted to lower temperatures (-135 - -154°C). Addition of 0.5 - 18% by weight of acetone lowered both the degree of conversion and the size of the thermographic peak. This proves that the liberation of heat is not due to the recombination of radicals. The mean rate of polymerization and the mean period of addition of one monomer molecule to the growing chain were calculated from the angle of inclination of the peak, and were found to be 0.009 - 0.018 m/sec and $8.6\cdot10^{-6}$- $1.6\cdot10^{-6}$ sec, respectively. The rates of polymerization indicate that acetaldehyde does not obey the laws of thermal explosion. Conclusions: (1) Solid-state polymerization between -134 and -153°C is dependent on the radiation dose; (2) the temperature shift is caused by more polymerization centers at higher doses; (3) at low temperatures, the reaction is very slow since the molecules are immobile;

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Gamma-induced solid-state ...

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(4) in the range of -140 to -150°C the molecular mobility increases and the reaction is accelerated; this is still promoted by the liberation of heat; (5) at higher radiation doses, an avalanche-like extension of the reaction occurs even at lower temperatures. The molecular weight is presumably lowered by an increase in the rate of chain rupture owing to the formation of active centers. There are 5 figures and 2 tables.

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

SUBMITTED: April 5, 1961

Card 3/3

NARYADCHIKOV, D.I.; GRISHINA, A.D.; BAKH, N.A.

Generation of electron paramagnetic resonance spectra during X-irradiation. Prib. i tekh. eksp. 7 no.3:192-193 My-Je '62. (MIRA 16:7)
(Paramagnetic resonance and relaxation) (X rays)

34479
S/020/62/142/004/016/022
B101/B110

11.1510
11.1360

AUTHORS: Larin, V. A., Grishina, A. D., and Bakh, N. A.

TITLE: Investigation of the mechanism of radiation oxidation and reduction by electron paramagnetic resonance

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 142, no. 4, 1962, 847 - 850

TEXT: The redox conversions of the pair methylene blue (MB) - leuco base of methylene blue (LMB) under the action of ionizing radiation was investigated by determining type and concentration of the free radicals by means of epr. The preparation of solutions of MB and LMB in methanol, acetone, and nitro-methane had been described earlier (DAN, 139, 406 (1961)). Gamma radiation was supplied by Co^{60} (1.25 Mev), Cs^{137} (0.60 Mev), or X-rays (0.08 Mev). The intensity was $3.2 \cdot 10^{14} - 5.5 \cdot 10^{15}$ ev/g·sec, the total dose $10^{17} - 10^{19}$ ev/g. The color change was measured with an СФ4 (SF4) or СФ2М(SF2M) spectrophotometer adapted for measurements in the range of 77 - 293°K. The epr spectra were recorded by means of an ЭПР-2 (EPR-2) radiospectrometer of the IKhF. Irradiation of samples and measurement of epr were conducted at 77 - 153°K. In $10^{-6} - 10^{-2}$ M oxygen-

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free solution of LMB, irradiation (at temperatures >77°K) led to formation of MB, the concentration of which increased linearly up to $\sim 10^{19}$ ev. The yield of MB increased with increasing concentration of LMB and increasing temperature. The life of the free radicals was shorter in methanol solution of LMB than in pure methanol. 10^{-6} - 10^{-4}M oxygen-free solutions of MB were discolored by irradiation. The reduction is reversible by supply of O_2 at room temperature. The radiation yield of the MB reduction is independent of temperature. The following conclusions are drawn from epr spectra and radical yields: (1) The epr spectrum of CH_3OH is a superimposition of $\dot{C}H_2OH$ and $CH_3\dot{O}$ spectra with the ratio 2 : 1. (2) LMB oxidation takes place through radiolysis products of the solvent in the presence of CH_3OH, predominantly through $CH_3\dot{O}$. (3) The experimental data are insufficient for interpreting the MB reduction. There is no dependence between concentration of radicals and oxidation. The temperature independence of this reaction suggests participation of hot H atoms and thermal electrons. (4) The radiation yields of radicals, determined by means of epr at 77°K, and the yields calculated on the basis of the redox reaction show $G(R)_{epr} \geq G(R)_{react}$ for the various solvents except for acetone for which $G(R)_{epr} = 1.4$ and $G(R)_{react} = 26$, which means that processes other than radical ones participate. Yu. B. Yakovlev and G. A. Semenova are thanked for taking the spectra. There are 4 figures, 1 table, and 11 references: 4 Soviet and 7 non-Soviet. The four most recent references to English-language publications read as follows: R. Smaller, M. S. Matheson, J. Chem. Phys., 28, 1169 (1958); R. S. Alger, T. H. Anderson, L. A. Webb, J. Chem. Phys., 30, 695 (1959); G. E. Adams, J. H. Baxendale, J. Am. Chem. Soc., 80, 4215 (1958); G. Meshitsuka, M. Burton, Radiation Res., 8, 285 (1958).

ASSOCIATION: Institut elektrokhimii Akademii nauk SSSR (Institute of Electrochemistry of the Academy of Sciences USSR)

PRESENTED: September 27, 1961, by A. N. Frumkin, Academician

SUBMITTED: September 25, 1961

37520
S/020/62/144/001/019/024
B124/B101

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AUTHORS: Bakh, N. A., Bityukov, V. D., Vannikov, A. V., and Grishina, A. D.

TITLE: Electric and paramagnetic characteristics of products obtained by radiation and heat treatment of polyethylene

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 144, no. 1, 1962, 135-138

TEXT: The conductivity of high-density polyethylene irradiated in vacuo at about 60°C with doses up to 10^{24} ev/g can be increased substantially by successive heat treatments at different temperatures up to 1000°C, thus leading to semiconductor materials. The powdered materials pressed between disk electrodes were investigated in vacuo ($\sim 10^{-5}$ mm Hg) and at temperatures ranging from -180 to +200°C. Conductivity was independent of both the grain size of the powder and the electrode material. In all cases, $\sigma_{20^\circ C}$ monotonically increased as the temperature of heat treatment was increased, i. e., from about 10^{-16} $ohm^{-1}cm^{-1}$ for unpyrolyzed irradiated polyethylene

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up to 10^{-1} $ohm^{-1}cm^{-1}$ for irradiated polyethylene samples preheated to 900°C, with some slowdown at 500 - 600°C and 10^{-9} to 10^{-8} $ohm^{-1}cm^{-1}$. The equation $\sigma = \sigma_0 e^{-\Delta E/2KT}$ (E = activation energy) is valid in the range of -25°C to +150°C, with ΔE being constant for each sample. The differential thermo-emf was related to copper. When the temperature of the sample was raised from 620 to 930°C, values of the thermo-emf between 250 and 4 μv/deg were obtained, with the sign of the thermo-emf corresponding to p-type conductivity in each case. The thermo-emf measured in vacuo is independent of the mean temperature of the sample between -50 and +150°C with ΔT=7 to 10°C. The presence of oxygen leads increases σ and the thermo-emf, and decreases ΔE down to a definite temperature which depends on the temperature to which the sample was previously heated. The experimental data obtained indicate that resistivity decreases with increasing frequency, the former having a constant value of $\sim 10^{12}$ ohms·cm at 5 - 12 Mc/sec; it is thus proved that the material under consideration is heterogeneous and contains regions of high conductivity which extend with increasing temperature of heat treatment. Structural changes in the

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polymer due to radiation and heat treatment were estimated from a study of the single-line epr. spectra (Figs.3 and 4). Both the concentration of paramagnetic centers and the line width were independent of the temperature of measurement. There are 4 figures and 1 table.

ASSOCIATION: Institut elektrokhimii Akademii nauk SSSR (Institute of Electrochemistry of the Academy of Sciences USSR)

PRESENTED: December 25, 1961, by A. N. Frumkin, Academician

SUBMITTED: December 20, 1961

Fig. 3. Concentration of paramagnetic centers as a function of the temperature of heat treatment. (1) $4.3 \cdot 10^{23}$; (2) $1.5 \cdot 10^{24}$; (а) air; (б) vacuum.

Fig. 4. Width of the epr spectral line versus the temperature of heat treatment; (а) in the presence of atmospheric oxygen; (б) vacuum $2 \cdot 10^{-5}$ mmHg, 2 hrs; (в) $5 \cdot 10^{-5}$mm, 2 hrs; (г) $5 \cdot 10^{-6}$mm, 24 hrs.

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S/020/62/145/002/014/018
B145/B101

AUTHORS: Revina, A. A., Aripdzhanov, Sh. A., and Bakh, N. A.

TITLE: Investigation into the formation of free radicals during the irradiation of palmitic acid and its derivatives with the epr method

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 145, no. 2, 1962, 363-365

TEXT: The authors studied the effect of the carboxyl group on primary processes in the radiolysis of carboxylic acids. Potassium salt and triglyceride were used besides free palmitic acid. Irradiation was conducted at -196°C (γ-radiation of Co^{60}, $\sim 5\cdot10^{16}$ ev/g·sec). The epr spectra were measured in vacuo and in the air. Solid α,α'-diphenyl-β-picryl hydrazyl was used as standard material. The spectra (width: 200 oersted) of samples irradiated with different doses showed differences in their relative band intensities. This proves the existence of different radicals and different rules in the kinetics of their accumulation. The 28-30 oersted doublet characteristic of carboxylic acids occurs in the

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spectrum of palmitic acid. The following radiation-chemical yields in vacuo (first figure) and in the air (second figure) were calculated from the linear increase in radical concentration with increasing radiation dose: palmitic acid 20, 20; tripalmitin 12, 7; potassium palmitate 9, 7 radicals per ev. The radical concentration was studied up to a radiation dose of $\sim 3 \cdot 10^{21}$ ev/g (for palmitic acid the concentration was $\sim 3 \cdot 10^{20}$ radicals per g), but no tendency toward a steady value was observed. Comparison with the results of A. Breger (J. Phys. Coll. Chem., 52, 551 (1948)) verifies connection between the primary radicals obtained and the processes yielding the final radiolysis products. Peroxy-type radicals were not found. There are 3 figures.

ASSOCIATION: Institut elektrokhimii Akademii nauk SSSR (Institute of Electrochemistry of the Academy of Sciences USSR)

PRESENTED: April 5, 1962, by A. N. Frumkin, Academician

SUBMITTED: April 3, 1962

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S/189/63/000/002/006/010
A057/A126

AUTHORS: Driyenovskiy, P., Bakh, N.A.

TITLE: Some products of radiolysis and radiative oxidation of acetone

PERIODICAL: Vestnik Moskovskogo universiteta, Seriya II, Khimiya, no. 2, 1963, 28 - 31

TEXT: In the Laboratoriya radiatsionnoy khimii (Laboratory for Radiation Chemistry) the formation of liquid products was investigated during the irradiation of acetone by X-rays with doses $(1.5 - 1.6) \cdot 10^{16}$ ev/cm^3 $\cdot$ sec. The experiments were carried out in a specially designed glass cell first with oxygen-saturated acetone and then with hydrogen (inert gas)-saturated acetone. Formaldehyde, acetyl acetone, and acids were determined after irradiation. Formaldehyde is formed from the start of irradiation in presence and absence of oxygen. A stationary concentration and dosis was observed in both cases but it was higher in the presence of oxygen, causing a drop in concentration of formaldehyde after irradiation. This effect was more pronounced with an increase of the dosis of irradiation and could attain 25 - 30% of the total effect 20 min after the

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end of irradiation. The initial yields of formaldehyde accumulation in presence and absence of oxygen were found to be 7.3 and 2.7 molecules/100 ev. Similar results were obtained for acetyl acetone, but in the presence of oxygen the yield is lower. Potentiometric titrations of the irradiated acetone indicate the formation of several acidic products. The titration curves at various irradiation doses are similar indicating the primary character of formation of all products. The total initial yield of oxygen-saturated acetone was $G \sim 10$ equiv./100 ev. The products formic and acetic acid are apparently contained in this case. The authors assume the participation of $\dot{C}H_3$, $CH_3\dot{C}O$, and $\dot{C}H_2COCH_3$ radicals in the formation of the final products of acetone radiolysis. Additional formation of formaldehyde in the presence of oxygen can be explained by the reaction: $\dot{C}H_3 + O_2 \rightarrow CH_3O\dot{O} \rightarrow CH_2 + OH$. A radical reaction can be assumed also for the formation of acetyl acetone: $CH_3\dot{C}O + \dot{C}H_2COCH_3 \rightarrow CH_3COCH_2COCH_3$. The investigations on the products of radiolysis of acetone have to be continued. There are 4 figures.

ASSOCIATION: Laboratoriya radiatsionnoy khimii (Laboratory for Radiation Chemistry)

SUBMITTED: August 2, 1961

RODER, M.; BAKH, N.A.; BUGAYENKO, L.T.

Redox transformations of acceptors in organic solvents induced by ionized radiations. Part 1: Transformations of iron chlorides in acetone solutions. Kin.i kat. 4 no.2:193-197 Mr-Ap '63. (MIRA 16:5)

1. Moskovskiy gosudarstvennyy universitet imeni M.V.Lomonosova, khimicheskiy fakul'tet.
(Iron chlorides) (X rays)

RODER, M.; BAKH, N.A.; BUGAYENKO, L.T.

Oxidation-reduction conversions of acceptors in organic solvents induced by ionized radiations. Part 2: Conversions of copper compounds in acetone solutions. Kin. i kat. 4 no.3: 353-356 My-Je '63. (MIRA 16:7)

1. Moskovskiy gosudarstvennyy universitet imeni Lomonosova, khimicheskiy fakul'tet.
(Oxidation-reduction reaction)
(Copper chlorides) (X rays)