33491

The use of radiocarbon (C^{14}) S/195/61/002/005/016/027
E030/E185

An unexpectedly interesting system is the decomposition of isopropyl alcohol on a vanadium trioxide catalyst. The catalyst was obtained by passing hydrogen over the trioxide at 417°. The general scheme possible is:

$$\begin{tikzcd} C_3H_6O & C_3H_7OH \arrow[l, "-H_2"'] \arrow[rr, "-H_2O"] \arrow[dr, "H_2"'] & & C_3H_6 \arrow[dl, shift left, "H_2"] \\ & & C_3H_8 \arrow[ur, shift left] & \end{tikzcd} \qquad \text{(III)}$$

By using radioactive propylene (up to 29 000 imp./min on $BaCO_3$), and by separating propane, propylene, and the catalysate, and determining their activities, it was shown that propylene is not converted to isopropyl alcohol at 315°, and that propane is formed, not from propylene, but from the isopropyl alcohol. There are 1 table and 10 references: 8 Soviet-bloc and 2 non-Soviet-bloc. The English language references read as follows: Ref.8: V.J. Komarevsky, J.Amer.Chem Soc., v.69, 238, 1947.

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33491

The use of radiocarbon (C^{14}) S/195/61/002/005/016/027
E030/E185

Ref.9: V.J. Komarevsky, Advances in Catalysis, v.9, N.Y., 1957, p.707.

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR
(Institute of Organic Chemistry imeni N.D. Zelinskiy, AS USSR)

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33492

11.0130Z

S/195/61/002/005/017/027
E030/E185

AUTHORS: Derbentsev, Yu.I., Balandin, A.A., and Isagulyants, G.V.

TITLE: Investigation of the role of cyclohexene in the heterogeneous catalytic dehydrogenation of cyclohexane, using radiocarbon

PERIODICAL: Kinetika i kataliz, v.2, no.5, 1961, 741-747

TEXT: The dehydrogenation of cyclohexane on chromia and rhenium catalysts has been studied, using C^{14}. Chromia was chosen as an oxide catalyst, favourable for doublet dehydrogenation, and rhenium as a metallic catalyst suitable for a sextet dehydrogenation, where the conversion rate of cyclohexene by this process is negligible. The chromium oxide in 2-mm pellets was obtained from ammonium bichromate. Before every experiment the rhenium catalyst, prepared by the method previously described (Ref.8: A.A. Balandin, Ye.I. Karpeyskaya, A.A. Tolstopyatova, Zh. fiz. khimii, v.33, 2471, 1959) was kept for one hour in hydrogen at 480 °C. A continuous flow reactor was used, with varying initial concentrations of cyclohexane (obtained by hydrogenation of benzol),

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Investigation of the role of S/195/61/002/005/017/027
E030/E185

benzol, and marked cyclohexene (activity 470 pulses/minute mg $BaCO_3$) obtained from C^{14} marked phenol. The catalysates were analysed chromatographically on a 7m long spiral column of diatomaceous earth, of which the first half was impregnated with dinonylphthalata, and the second half with dioctylsebacate. the outlet from the column was led either to a thermal conductivity detector or for quantitative analysis to a bubbler with obaryta water, in order to obtain barium carbonate. The radioactivity of targets made from this carbonate was measured with an end window counter, and samples taken after 15 min. On the chromia catalyst, benzole was formed by a parallel-consecutive process. conversion of cyclohexane into benzole is 1.5 times faster than the conversion of cyclohexene; a considerable part being formed from adsorbed and desorbed cyclohexene and it is obviously a doublet mechanism of dehydrogenation. On the rhenium catalyst, there is no consecutive process at all and cyclohexane is converted directly into benzole by a sextet mechanism. The differing behaviour on the two types of catalyst is striking. on chromia it is dehydrogenated to benzole, but on rhenium it is
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hydrogenated back to cyclohexane. Acknowledgments are expressed to Ye.I. Karpeyskiy for the rhenium catalyst. Ye.N. Komarova and V.S. Livshits participated in the tests.
There are 5 figures, 4 tables and 20 references: 15 Soviet-bloc and 5 non-Soviet-bloc. The four most recent English language references read as follows:

Ref. 3: H.H. Long, J.C.W. Frazer, E. Ott, J.Amer.Chem.Soc., v.56, 1101, 1934.
Ref. 4: P.H. Emmett, N. Skau, J.Amer.Chem.Soc., v.65, 1029, 1943.
Ref.11: H.S. Taylor, J.Amer.Chem.Soc., v.60, 627, 1938.
Ref.13: E.F.G. Herington, E.K. Rideal, Proc.Roy.Soc., London, v.A190, 289, 1947.

X

ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo AN SSSR
(Institute of Organic Chemistry imeni N.D. Zelinskiy, AS USSR)

Card 3/3

Decomposition reactions in the process of catalytic hydrogenation in presence of nickel. Role of the catalyst in hererogeneous catalysis. A.A. Balandin (J. Russ. Phys. Chem. Soc., 1930, 62, 703-728).- An empieical rule is given, the useof wjich allows the products of catalytic hydrogen oforganic substances to be predicted. If the values 1,2,3, and 4 be assigned to the e elements halogen, oxygen, nitrogen, and carbon, and if be taken to represent the product of the numbers assigned to any pair of these elements, then the facility with which the linking between the two elements is broken in the catalytic hydregenation of the compound is inversely proportional to the value of . This rule is shown to hold for a large number of compounds; the most frequent exceptions to it are to be found amongst compounds containing the carbonyl group, which often eliminate carbon monoxide without reduction, and amongst heterocyclic compounds possessing nitrogen in the ring. The explanation of the above rule is not to be found in the energy change associated with the formation of the linkings in question, or in the affinity between hydrogen and the respective atoms of a given pair. The same order is found for the a above four elements for a series expressing facility of replacement of the g given element from its compound with nickel by a different element in combin-ation with hydrogen. The readiness with which an atomic group is separated during the catalytic hydrogenation of a compound is the greater the greater is its affinity to the catalyst, and is the smaller the greater is its affinity to the remainder of the molecule; for this reason the stability of a given linking in the absence of a datalyst need not be the same as in its presence.

R. Truszkowski.

PROCESSES AND PROPERTIES INDEX

Ca

10

Natural classification of catalytic reactions in organic chemistry. I. Compounds of carbon, hydrogen and oxygen of constant valency with single and double bonds. A. A. BALANDIN. *J. Gen. Chem.* (U. S. S. R.) 2, 160-82(1932); cf. *J. Russ. Phys.-Chem. Soc.* 61, 909(1929); *C. A.* 23, 2872; Polanyi, *C. A.* 23, 5095.—The natural classification of org. catalytic reactions is deduced from the theory of multiplets and is based on the assumption that in complex mols. only those atoms interact which are in direct contact with each other during the reaction. The classification exhausts all stoichiometrically possible cases of catalysis, thereby limiting the no. of classes and types of catalytic processes, and takes into account the chem. nature of reacting atoms and the nature of disrupted and newly formed bonds. Therefore to every type can be ascribed certain combinations of catalytic substances which must be found experimentally, and the obtained values computed as was done in the case of Ni (*C. A.* 23, 5090). The knowledge to which catalytic substances and under what conditions the required indexes are related would make possible the selection of the catalyst for a given reaction, which is the ultimate object of the investigation. Here the work was confined to C, H and O of const. valence with single and double bonds, and to consideration of only double indexes I_2, *i. e.*, the simple and common reactions in which 2 bonds become split and newly formed. From 6561 possible combinations there remain 79 types divided into 9 classes according to the atoms given in the index. The results are shown in tables. The work is being continued.

CHAS. BLANC

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

2

A logarithmic relation between the constants of the formula of Arrhenius. A. A. Balandin. J. Phys. Chem. (U. S. S. R.) 4, 257-67(1933); cf. C. A. 27, 1262.—Rate of dehydrogenation of cyclohexane was detd. by H_2 evolved and by change of n. In the equation $k = k_0e^{-Q/RT}$ the relation $Q/\log k_0 = (2.0 \pm 0.2)\cdot10^4$ holds for dehydrogenation on Pt, Pd, Ni and Os catalysts of decahydronaphthalene, cyclohexane, cyclohexanol, piperidine and cyclohexanone, on charcoal, asbestos, TiO_2 or Al_2O_3 carriers, although Q and k_0 vary several times for different substances and different catalysts at temps. of 170-300°.

F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

PROCESSES AND PROPERTIES INDEX

10

Preparation of butyl and hexyl alcohols from by-products obtained in the synthesis of divinyl from ethyl alcohol. III. B. A. Kazanskii, A. A. Balandin, I. M. Tverkovnikov, K. A. Ivanova and E. N. Staroverova. *J. Applied Chem.* (U. S. S. R.) 6, 260-73(1933).—The Bu fraction sepd. from the above by-products b. 115-20°, d_4^{20} 0.8332, n_D^{20} 1.4085, Br no. 60.3; it constituted about 22.18% of the unsatd. alcs. of the formula C_4H_8O in the fraction. This fraction was hydrogenated by the Sabatier method in the presence of various catalysts, such as Ni pptd. on pumice stone with a glass and a Cu tube, Cu on asbestos, Fe, and Ni (hydrogenation in the liquid phase). The process was carried out at 340-80°, 230-30°, 120°, 300°, 200-5°, 400-60° and 100°. The catalyzate had the following consts.: b_{745} 115.5-17° (mainly 116-17°), n_D^{20} 1.4098, d_4^{20} 0.8103, which are fairly close to those given in the literature for BuOH. The hexyl fraction was also redistd. and hydrogenated under similar conditions. It yielded a product b. 150-5°, n_D 1.4187, d_4^{20} 0.8285. This is not a uniform product. The yield of BuOH amounted to 19.2% of the total of the alc. by-products. The best hydrogenation temp. for the Bu fraction lies at 120°, although hydrogenation takes place at 80°; Ni pptd. on asbestos is the best catalyst at 180°.

A. A. B.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

2

Catalytic oxidation of butyl alcohol to butyraldehyde. A. M. Rubinshtein, A. A. Balandin, B. A. Dolgoplosk, K. A. Morozov and L. I. Vasil'evskaya. *J. Applied Chem.* (U. S. S. R.) 6, 278-89 (1933).—The oxidation was effected with air and with CO_2, the following catalysts being investigated: (1) Cr_2O_3 catalyst in a brass tube, (2) Cr_2O_3 + MnO_2 (35:65) in a brass tube, (3) CuO, (4) Cr_2O_3 + Fe_2O_3 (1:3) in a brass tube, (5) MnO_2 in a brass tube, (6) MnO_2 + Fe_2O_3 (2:3) in a brass tube, (7) Fe_2O_3 in a brass tube, (8) fused V_2O_5, (9) Ag (40%) on asbestos, (10) Ag (60%) on asbestos, (11) Ag (75%) on asbestos, (12) Ag (80%) on asbestos obtained by pptg. Ag on asbestos with HCHO from NH_3-$AgNO_3$, (13) Ag gauze in a glass tube, (14) Cu (7.5%) + Ag(42.5%) on asbestos, and (15) Cu (25%) + Ag (25%) on asbestos (50%) prepd. as in (14). The reaction is accompanied by evolution of heat (with the Ag catalyst); the catalyst, however, retains its activity. With 60-75% of Ag pptd. on asbestos there is no change in the yield of aldehyde and acid. Water improves the process and the best temp. for all Ag catalysts is 350-80°. The most efficient catalyst is Ag (80%) pptd. on asbestos with HCHO. The yields of aldehyde and acid were, resp., as follows, with air as oxidant: with finely pptd. Ag 72 and 4%, finely pptd. mixt. of Ag and Cu on asbestos 68 and 7%, with (8) 49 and 22%, with (7) 40.7 and 6.9%, with (5) 31 and 0.3%. The highest yields were obtained with a Ag catalyst, a furnace temp. of 350-60° and an air velocity of 1-1.5 l. per min. through a tube 15 mm. in diam., the alc.-water mixt. (2:3) being preheated to 85-90°. The temp. is lower for a Ag-Cu catalyst by 25-50°; for V_2O_5 it is about 400° and for Fe_2O_3 400-500°. The Cr_2O_3, Cr_2O_3 + MnO_2 and CuO catalysts in sticks procured from Kahlbaum were useless. Expts. on the oxidation of BuOH with CO_2 in the presence of V_2O_5 were quite successful when made at 500-50° and at an alc. temp. of 80-95°.

A. A. Boehtlingk

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

SA

837. Formation of Butadiene and Acetylene by H.F. Discharges on Ethylene. A. Balandin, J. Eidus and N. Zalogin. *Comptes Rendus de l'Acad. des Sciences, U.S.S.R.* 4, *pp.* 133–137, *Oct.* 21, 1934. *In German.*—In a closed system, ethylene containing a little hydrogen is completely condensed after 10 hours by the action of h.f. discharges, the gaseous phase containing 67 % hydrogen and 30 % of saturated hydrocarbons (5·3 % methane), and the condensation product being a dark oily liquid of molecular weight about 500. Acetylene was not detected, since it takes part in the reaction. An induction period was observed which is shortened by the presence of water-vapour. In a circulating system at atmospheric pressure, a volume contraction was observed which altered almost linearly with time, and butadiene together with maleic anhydride were formed, the former in amounts dependent on the circulation velocity and partial pressure of hydrogen in the exit gas. The results indicate a chain mechanism for the reactions.

H. H. Ho.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

ca

2

Kinetics of the catalytic dehydrogenation of methylcyclohexane on a nickel-aluminum oxide catalyst. A. Balandin and N. I. Shuikin. *Acta Physicochim. U. R. S. S.* 1, 300-11(1934)(in German).—By the same method as for dimethylcyclohexane (*C. A.* 28, 7127[9]) the energy of activation for mixts. with 0-90% toluene is 12,30[illegible] cal. and the value of k_0 in the equation of $k = k_0 e^{-[illegible]/T}$ is 8.8 × 10[illegible] in the temp. range 300-83°. Decompn. with methane formation is negligible except in the toluene-rich mixts. The toluene half period of adsorption is greater than that for methylcyclohexane and slightly decreases the rate of dehydrogenation. The catalyst was prepd. by reduction of the mixed oxides dried at 120° (Zelinski and Kommarevski, *C. A.* 18, 2088) by first dehydrating at 250° and then slowly raising the temp. to 330° over a period of 30 hrs. The activity of the catalyst is slightly less than that of pure Ni reduced at lower temp. but retains its activity much longer. The velocity of reaction is slightly greater than for cyclohexane.

F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

Free radicals in the process of pyrolysis and in the electrical discharge. A. Balandin and A. Lieberman. *Uchenye Zapiski (Moscow State Univ.)* 2, 209-11(1934); *Chem. Zentr.* 1935, II, 1686.—By means of a modified Paneth-Rice arrangement it was shown that in the pyrolysis of *isoamyl alc.* in a quartz tube at 700-800° free radicals were formed; their presence was detected by the disappearance of a Ag mirror. Upon increasing the temp. to 1100-1200° the Ag mirror remained unchanged and a resinous ppt. was deposited in the neighborhood of the heating unit. When ethane was led through a glow discharge at 0.3 l. per min. the Ag mirror remained unattacked; H_2 and resin gradually were formed. Apparently the excess supply of energy produced a further decompn. as well as a complicated reciprocal effect in the free radicals formed, which would indicate a limit of the possibility of detecting such radicals.

M. G. Moore

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

CA

18

The formation of nitrogen dioxide from nitrogen and oxygen in a high-frequency discharge. A. A. Balandin, Ya. I. Eidus, N. Sikgin and V. Verpakovskii. *Wiss. Ber. Moskau. Staats-Univ.* 2, 213-16(1934); *Chem. Zentr.* 1936, I, 2932. NO_2 is formed in a mixt. of O_2 and N_2 under the influence of the high-frequency discharge. In expts. in a closed system without circulation of the gases it was shown that, following a break in pressure, a gradual decrease in it takes place; after 1.5 hrs. under the given exptl. conditions the pressure begins to increase, with the simultaneous formation of brown NO_2 vapors. In a closed system, with circulation of the gas, the NO_2 was frozen out and identified by its m. p. The velocity of formation of NO_2 from a stoichiometric mixt. of N_2 and O_2 is about 5 times as great as from air.

M. O. Moore

ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

The relative life periods of ethyl alcohol and acetaldehyde molecules on the surface of a copper catalyst. A. Balandin and A. Bork. *Uchenui Zapiski (Moscow State Univ.)* 2, 217-20(1934); *Chem. Zentr.* 1935, II, 1528. The dehydrogenation velocity of EtOH in the presence of MeCHO on a Cu catalyst was measured. By use of an equation previously developed (Balandin, *Arbeiten der III Phys.-Chem. Konf.*, L. 193 (1930)) for kinetics in streaming gases and the Langmuir adsorption theory it was shown that under the conditions of the expts. the MeCHO mol. remains on the surface of the catalyst 5 times as long at 270° and 3 times as long at 240° as the EtOH mol. The method is thus considered suitable for the detn. of the relative life periods of the mols. M. G. Moore

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

The orientation of molecules of secondary alcohols during dehydrogenation catalysis. A. Balandin, M. Marushkin and B. Ikonnikov. *Uchenye Zapiski (Moscow State Univ.)* 2, 231-4(1934); *Chem. Zentr.* 1935, II, 1528. The reaction velocities of dehydrogenation of *isopropyl alc.* and *cyclohexanol* at 230-70° on a Cu contact were shown to be the same. From this it is assumed that both mols. are attracted to the Cu surface by the HOHC < group. Special expts. showed that the ketone formed is almost as strongly adsorbed at the surface of the catalyst as the alc. M. O. Moore

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

The catalytic reduction of p-chloronitrobenzene. A. Balandin and A. Tikova. *Uchenye Zapiski (Moskov. State Univ.)* 3, 229-31(1934); *Chem. Zentr.* 1935, II, 1580.- On the basis of the multiplet theory of heterogeneous catalysis (cf. *C. A.* 23, 2872) it is to be expected that on a metallic Ni surface the N-O linkage is more easily broken and hydrogenated than the C-Cl one. In substantiation of this assumption it was found that in the hydrogenation of p-chloronitrobenzene in the presence of Ni at 220°, chloroaniline was first formed and no nitrobenzene. M. G. Moore

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

10

The catalytic preparation of ethyl alcohol by the hydration of ethylene. A. Balandin and M. Nesvizhskii. Uchenie Zapiski (Voronezh State Univ.) 7, 223-8(1934); Chem. Zentr. 1935, II, 1828; cf. C. A. 27, 223.—When C_2H_4 and water vapor (with admixt. of air) was led over activated C at 180° which had been impregnated with 70% H_2SO_4 (with the addn. of Ag_2SO_4) a 3% yield of EtOH was obtained without noticeable side reactions occurring. Calcns. were based on the C_2H_4. A disadvantage of the process is the fatiguing of the catalyst. M. G. M.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

10

The catalytic addition of hydrogen chloride to ethylene. A. Balandin and O. Livanova. *Uchenuie Zapiski (Moscow State Univ.)* 2, 237-9(1934); *Chem. Zentr.* 1935, II, 1898.—By detn. of the decrease in pressure it was found that the addn. of HCl to C_2H_4 in the presence of $BaCl_2$ amounted to 62%. No reaction was observed under 210°, while above 300° decompn. of the EtCl occurred.

M. O. Moore

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

1a

2

Kinetics of the catalytic dehydrogenation of dimethyl-
yclohexane. A. A. Balandin and Yu. K. Yur'ev. J.
hys. Chem. (U. S. S. R.) 5, 393–400(1934).—The speed
f the reaction on Ni and Al oxide catalysts was studied
s a function of temp. and of the initial concns. of the di-
ethylcyclohexane (I)—xylene (II) mixts. (consisting
 both cases of all three isomers). For all mixts. contg.
0–100% I the energy of activation from 280° to 350° is
,700 cal. per mol. but falls to 12,300 in a 10% mixt.
ethane formation is slight if I is pure. The rate of de-
ydrogenation of I is slightly greater than that of cyclo-
exane. The analyses were made by means of refractive
dexes, which are practically a linear function of the
ompn. of the mixt. of I and II. F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

BC

A-3

PROCESSES AND PROPERTIES INDEX

Classification of catalytic reactions in organic chemistry. II. Method of finding a complete system of doublet reactions and the calculations for the atoms H, C, N, O, S, Cl and the linkings from 0 to 4. A. A. Balandin (J. Phys. Chem. U.S.S.R., 1934, 5, [illegible]).—By means of a matrix formulation a possible 810,000 compounds are classified in such a way that reactions can be generalised by means of classification symbols. The method is applied particularly to hydrogenation.

CH. ABS. (r)

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

CA

2

The comparative action of mixed catalysts in the simultaneous dehydration of ethyl alcohol and ammonia N.I. Shuikin, A.A. Balandin and Z.I. Plotkin. J. Gen. Chem. (U.S.S.R.) 4, 1444-50 (1934).- The dehydrating action of mixed catalysts contg. Al_2O_3 with one other oxide was compared with that of pure Al_2O_3. The dehydration of 1:1 mol. mixt. of EtOH and NH_3 was studied. The mixed catalyses contained 10% Fe_2O_3, 20% Cr_2O_3, 10% SnO and 10% ZnO, resp. the reaction temps. were 300°, 330°, 360°, and 400°. The reaction vessel was a glass tube 15 mm. in diam. contg. a layer of catalyst, dried at 150°, 30 cm. long. The NH_3 was introduced at a rate of 55 -60 cc./ min. and the alc at 1.6 cc./10 min. In each expt. 20 cc of alc. was passed. In 2 expts. C_2H_5N derivs. were formed. With Al_2O_3 - Fe_2O_3 at 360° and 400° the yield of amines was the same as with Al_2O_3. In the case of all the other mixed catalysts the rate of amine formation was lower and the rate ~~of olefine formation~~ of alc. dehydration higher. The properties of the mixed catalysts cannot be regarded as a summation of the properties of the component oxides.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

10

Catalytic preparation of butyl acetate and butyl butyrate

M. B. Turova, A. A. Balandin, M. S. Merkurova and M. V. Guseva. *J. Applied Chem.* (U. S. S. R.) 7, 1454-60 (1934).—The catalyst used in the process was prepd. from activated C which was preliminarily treated with alkali and strong HNO_3, followed by removal of nitrate, drying at 110-120°, impregnating with H_3PO_4 (d. 1.3) (60 cc. acid per 35 g. C) and heating for 3 hrs. to red heat in a continuous stream of N_2, thus leaving 35% of H_3PO_4 in the C. The BuOH was obtained from the synthetic rubber plant (Lebedev method) and it was hydrogenated to convert the unsatd. alcs. present. It then b. 116-18°, n_D^{20} 1.4010, d_4^{20} 0.8137. It was found that: (1) the yield of the ester decreases very little when increasing the feeding velocity from 0.07 to 0.5-0.6 cc. (4-6 to 50-60 drops) per min. at a process temp. of 150°, while the ester yield is considerably increased at 210° with increase in the feeding velocity. A 100% and 88% AcOH produces similar results, while the ester yield is immediately greatly reduced with 30% and 18% acids. A 96.87% yield of the ester was obtained under the above conditions, when using 6 equivs. of acid to 1 equiv. of alc., and the catalyst did not show any deterioration in the entire series of expts. In the *esterification of PrCO₂H with BuOH* the highest yield of the ester (83.43%) was obtained when using 2 equivs. of acid per equiv. of BuOH, at a temp. of 180° and a feeding velocity of 10-12 drops per min. An increase of the temp. at const. feeding velocity lowers the yield, while an increase of the feeding velocity at 150° affects the yield very little. At 210° an increased feeding velocity raises the yield. The catalyst used in the 1st expts. was used again without any reactivation. A. A. Boehtlingk

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

BC

a-1

Structure theory of chemical change. Complete system of doublet reactions. A. A. BALANDIN (Acta Physicochim. U.R.S.S., 1935, 2, 177—202; cf. A., 1930, 519, 890).—A complete system of "doublet" reactions in org. chemistry is drawn up. All have not been experimentally realised. The theory of structure of reactions may also be applied to heterogeneous reactions. Hydrogenation reactions are more fully discussed. A. J. M.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

2

PROCESSES AND PROPERTIES INDEX

Directions of reactions of decomposition and condensation. A. A. Balandin. *Acta Physicochim. U. R. S. S.* 3, 343-[illegible] ([illegible])(in English).—Theoretical. The theory of reactions based on the multiplet theory is developed along the line of detg. according to the doublet scheme the totality of the directions followed by the reaction of a mol. [illegible] and unimol. reactions and the effects of symmetry are considered. The results are applied to the cases of HCHO reduction, EtOH-MeCHO union, and Me[illegible]N decompn. F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

BC A-1

Application of the structure theory of reactions to Lebedev's synthesis of butadiene from alcohol and to Rice's theory of pyrolysis. A. A. BALANDIN (Acta Physicochim. U.R.S.S., 1936, 2, 3[illegible]—376).—The author's theory (cf. preceding abstracts) is applied to the catalytic decomp. of EtOH at 480°, with special reference to the formation of $(CH_2:CH)_2$. Rice's theory of thermal decomp., which is in accord with the doublet mechanism of decomp., is developed and applied to cyclic hydrocarbons. The results are in qual. agreement with experiment.

J. W. S.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

4

Chemical effects of high-frequency electric discharge on a nitrogen-oxygen mixture. A. A. Balandin, Ya. I. Fidus and N. G. Zalogin. *J. Phys. Chem.* (U. S. S. R.) 6, 301-[illegible](1935).—The formation of oxides of N in O-N mixts. subjected to a high-frequency elec. discharge takes place by a chain mechanism. The primary products are ozone and N_2O_5, the latter then decompg. into NO_2 and O_2. The energy input for 1 kg. HNO_3 is [illegible] kw. hrs., and the efficiency of the elec. discharge is 0.0[illegible]%.

Zelikow

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

CA

2

A study of the parallel reactions of dehydration and dehydrogenation on mixed catalysts. A. A. Balandin and A. M. Rubinshtein. *J. Phys. Chem.* (U. S. S. R.) 6, 576-89(1935).—Mixed Ni-Al oxide catalysts were prepd. from various combinations of the sulfates, nitrates and chlorides with varying amts. of NaOH or Na_2CO_3 as pptg. agents. The final products as catalysts for dehydrogenation and dehydration of isoamyl alc. and the decompn. of AcH ranged from very active to totally inactive and the relative proportions of the products obtained varied widely. For dehydrogenation the energies of activation ranged from 8800 to 22,400 cal.; for dehydration from 15,000 to 33,000 cal. and for aldehyde decompn. from 17,000 to 47,000 cal. A catalyst very active toward one reaction was not necessarily active toward another, and no parallelism exists between the orders of the activation energies of various catalysts for different reactions. No great difference in activity was found as a factor of the anion in the original salt used, but the sulfate catalysts gave higher energies of activation in general. The value of $Q/\lg k_0$ in the Arrhenius equation was 1.83 for dehydrogenation and 3.71 for dehydration with a variation of only 25% for all of the 9 catalysts used. F. H. Rathmann

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

BA[illegible]

Present position of the pro[illegible] of catalysis and the theory of multiplets. A. [illegible]alandin. *Uspekhi Khim.* 6, 1004-87(1936).—The dev[illegible]ment of the multiplet theory of catalysis on the ba[illegible] of data obtained by B. and by others (cf. *C. A.* 23, [illegible]2, 8080; 24, 4084, 5585) is discussed, and new unpubli[illegible]d data are added. The multiplet theory is applied t[illegible] both the phys. and the chem. aspects of catalysis. [illegible]Quantum-mechanically its foundations were strengthene[illegible] by Polanyi (cf. *C. A.* 23, 5048). The shapes of mols. [illegible]ring dehydrogenation and hydrogenation catalysis and o[illegible] the corresponding crystal lattices of the catalysts are co[illegible]sidered on the basis of new work. Energetic factors are [illegible]taken into account. The theory predicts the course of [illegible]atalysis for various chem. bonds. A complete system o[illegible] doublet reactions is given, and serves for classification [illegible]purposes. As an example, by its help the as yet unknow[illegible] reactions of the hydrogenation hydrolysis of acid *N*-[illegible]omenanides are predicted. The results are generalized t[illegible]a structural theory of reactions and a consideration of th[illegible] structure theory of complexes. Index groups of atoms in co[illegible]tact with the catalyst are distinguished. Specific catal[illegible]is depends on their orientation to the catalyst. The p[illegible]blem of studying the relation of these indexes to the a[illegible]logous functional groups of the classical structure theo[illegible] is presented. Reptl. examples of such studies on t[illegible] hydration, amination and alkylation (cf. *C. A.* 27, 22[illegible] 30, 943[illegible]) are brought forward. The math. theory o[illegible] the direction of decompn. and of condensation of molecules is considered (cf. *Acta Phys. Chem.* 2, 177(1935); *C. A.* 29, 6494[illegible]). By this means the multiplet theory is applied to the synthesis of bivinyl from alcs. where up to C_6 about 20 different products are formed. The most recent data (*C. A.* 29, 4333[illegible]) also are in accord with the theory. The kinetics of heterogeneous catalysis of dehydrogenation and of hydrogenation are considered on the basis of work by the author and his co-workers (*C. A.* 27, 1262; 28, 2255[illegible], 30, 3306[illegible]; *Acta Physicochim. U. R. S. S.* 1, 184(1934); *C. A.* 29, 6130[illegible]).

A. A. Balandin and
F. H. Rathmann

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

BC

a-3

Influence of substituents on the velocity of catalytic dehydrogenation of cyclohexane derivatives. II. A. A. BALANDIN and N. I. SHUIKIN (Sci. Rep. Moscow State Univ., 1936, No. 6, 251—256).—The velocity of dehydrogenation of methylcyclohexane at 200—250° (Ni-Al_2O_3 catalyst) is slightly > that of cyclohexane. R. T.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

CA

2

Kinetics of thermal decomposition of potassium formate. A. A. Balandin, L. Kh. Freidlin and D. N. Vaskevich. *Sci. Repts. Moscow State Univ.* 1936, No. 6, 321-45. HCO_2K (I) yields chiefly K_2CO_3 (II) at 370-425° and chiefly $K_2C_2O_4$ (III) at 440-475°; both reactions proceed simultaneously at 420-440°. The energy of activation of the former reaction is 10 times that of the latter. The ratio II/III of the product falls when less than 27% of glass is added to the I and then rises rapidly to a max. for 10:1 glass-I mixts., at 440°; the ratio is at a min. for 0.8:10 III-I, or 3:10 II-I mixts., at 405°. The process is represented as 2I → OHCH(OK)CO_2K(IV) → III + H_2; IV → II + CH_2O; CH_2O → CO + H_2. B. C. A.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

A 54

A

3299. Chemical Reactions between Nitrogen and Oxygen in H. F. Discharge. A. A. Balandin, J. T. Kidus and N. O. Zalogin. *Acta Physicochimica*, [illegible], pp. [illegible]–304, 1936. *In German.*—The formation of nitrogen oxides from N_2–O_2 under the influence of h.f. discharge is investigated. At first O_3 and N_2O_5 form and collect; later the decomposition of O_3 is accelerated. When the velocity of decomposition attains a maximum value, N_2O_5 begins to change into NO_2. The reactions run in accordance with a chain mechanism.

J. K.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

BC

A-1

Free atoms and molecular dissociation in high frequency discharges. A. A. BALANDIN and J. EIDUS (Acta Physicochim. U.R.S.S., 1936, 4, 537—546).—The instantaneous pressure increase on starting a high-frequency discharge was studied for discharges through a no. of pure and mixed bimol. gases and Ne. The effect, observed with all bimol. gases, is dependent on the nature of the electrodes, the initial pressure of the gas, and the current and voltage in the secondary. No effect is observed with Ne. The presence of H atoms in the discharge through H_2 is indicated by the reduction of MoO_3 in the discharge tube. O. D. S.

METALLURGICAL LITERATURE CLASSIFICATION

CA

9

Heterogeneous catalytic decomposition of ethyl alcohol. A. A. Balandin. *J. Phys. Chem.* (U. S. S. R.) 7, ... (1936). B. cites the work of Lebedev, Gorin and Khutoretskaya (C. A. 30, 4325) on the effect of the addn. of C_2H_4, H_2O, BuOH, Et_2O and AcH to alc. on the prepn. of butadiene. In the last case the yield of butadiene is increased from 15 to 25% of theory. B. points out that the effect of each addendum can be predicted by means of his doublet theory of reactions (cf. C. A. 30, ...).

F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

Ca

2

Reaction between sodium formate and sodium hydroxide. A. A. Balandin and L. Kh. Freidlin. *J. Gen. Chem.* (U. S. S. R.) 6, 868-72(1936). The thermal interaction of alkali salts of monobasic aliphatic acids with caustic alkalies with the formation of hydrocarbons was studied. $NaCO_2H$ and NaOH in various proportions were charged into a 5-cc. ampoule, the top of which was drawn to a delivery tube ending in a capillary and connected with a water-jacketed gas buret. The ampoule was electrically heated in a bath of an equal mixt. of KNO_3 and $NaNO_3$. The temp. was kept const. within ± 0.5° by an elec. regulator. The gaseous and solid reaction products were analyzed (cf. *J. Applied Chem.* (U. S. S. R.), in press). The reaction begins at 210° and proceeds rapidly at 250°. The reaction gives pure H and no CO. With NaOH in an equiv. or higher ratio, the solid reaction product consists of Na_2CO_3. With NaOH in less than equiv. amt. in addn. to Na_2CO_3 there is formed $Na_2C_2O_4$, increasing with the decreasing ratio of NaOH and increasing temp. At temps. below about 270° no $Na_2C_2O_4$ is formed regardless of the amt. of NaOH added. $Na_2C_2O_4$ also reacts with NaOH with the formation of Na_2CO_3 and H. The reaction begins at 260° and proceeds at an unusually high rate at 310°. The probable scheme of decompn. is: (1) $NaCO_2H + NaOH \rightarrow Na_2CO_3 + H_2$; (2a) $2NaCO_2H \xrightarrow{\text{NaOH catalyst}} Na_2C_2O_4 + H_2$; (2b) $Na_2C_2O_4 + 2NaOH \rightarrow 2Na_2CO_3 + H_2$. The difference between schemes 2 and 1 is that the reaction proceeds in 2 stages with the NaOH acting as a catalyst in a and as a reacting component in b, with the $Na_2C_2O_4$ as the intermediate product. The results of decompn. of $Na_2C_2O_4$ with NaOH confirm this supposition. Chas. Blanc

ASD-SLA METALLURGICAL LITERATURE

CA

2

Kinetics of consecutive parallel first-order reactions. A. A. Balandin and D. N. Vaskevich. *J. Gen. Chem.* (U. S. S. R.) 6, 1870-7(1936). – A math. discussion of the kinetics involved in consecutive parallel first-order reactions, using as a concrete example the simplest case $D \xleftarrow{K_1} A \xrightarrow{K_2} B \xrightarrow{K_3} C$.

S. L. Madorsky

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

Mechanism of the decomposition of hydrazones and the theory of multiplets. Kinetics of the catalytic decomposition of cyclohexylidenehydrazine hydrate. A. A. Balandin and D. N. Vaskevich. *J. Gen. Chem.* (U. S. S. R.) 6, 1878-81(1936); cf. *C. A.* 30, 4079[9]. The multiplet theory of catalysis requires that the Kishner-Wolff reaction (cf. *C. A.* 7, 790) for the formation of hydrocarbons by decompn. of hydrazones on a Pt catalyst pass through the intermediate stage of diimine formation. By use of the kinetic method of parallel consecutive reactions, described previously (cf. preceding abstr.), it is experimentally found that the decompn. of cyclohexylidenehydrazine hydrate (I) on Pt or KOH catalyst to cyclohexane (II) actually passes through such an intermediate stage. The diimine (III) is very unstable with a half-time period of 34.8 sec. at 180°. The reaction-rate consts. for the formation of III, its decompn. to II, and for the formation of cyclohexanol (IV) are detd. and the reactions shown to be first order. By variation of exptl. conditions the decompn. of I may be directed to yield chiefly IV. Energies of activation for the catalysts used are: Pt 43,800 cal./mol.; Pt + KOH (1:10) 18,300, Pt + KOH (1:80) 12,600, KOH 20,300. In the absence of catalyst I slowly changes to dicyclohexylidenezine. John Livak

γ

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

"Catalyse de deshydrogenation du cyclohexane en presence de l'oxyde de chrome." Balandine, A. A. (p. 18)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii). 1937, Volume 7, No. 1.

APPROVED FOR RELEASE: Wednesday, June 21, 2000 CIA-RDP86-00513R00010

PROCESSES AND PROPERTIES INDEX

Calculation of the intermediate equilibria in catalytic kinetics and the geometry sites. A. A. Balandin. *Compt. rend. acad. sci. U. R. S. S.* 26, 741-7 (1939) (in English) --Math. General expressions are given in terms of equil. consts. for the equil. concns. in systems of any no. of components involving any given intermediate states.

A. O. Allen

2

N. D. Zelinskiy Lab. Organic Chem., Section of Organic Catalysis, Moscow State U.

ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA 2

Chemistry and structure. II. Elements of higher dimensions. Models, representing the configuration and the movements of molecules and their application. A. A. Balandin. *Bull. acad. sci. U. S. S. R., Classe sci. chim.* 1948, 371-84; cf. *C. A.* 34, 7071[4].—Theoretical math. The application of structural matrices is discussed. "Its application involves the molar refraction, the energy of [illegible], the vibration const. of the Raman spectrum, the size of the mols., the dipole moments, the planes of crystal lattices, the multiplet schemes and the topological reaction isomerism." James J. Lichtin

Inst. Organic Chem., AN SSSR

ASD-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

B C A

Thermal transformations of thallium formate. L. C. Freidlin, A. A. Balandin, and A. I. Lebedeva (Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim., 1940, [illegible]).—The reactions (i) $2HCO_2Tl$ (I) → $Tl_2CO_3 + CO + H_2$, (ii) 2(I) → $2Tl + 2CO_2 + H_2$, (iii) 2(I) → $2Tl + CO_2 + HCO_2H$ take place at 210—270°; reactions (ii) and (iii) are favoured by rising temp. and by dehydrogenation catalysts (Pt-black, Co-asbestos). Oxalate is not produced under any conditions. (I) reacts with $NaNH_2$ at 97° or CaO at 130—230° as follows: 2(I) + $2NaNH_2$ → $NaHCN_2 + NaOH + Tl_2CO_3 + H_2$; 2(I) + CaO → $CaCO_3 + 2Tl + H_2$, whilst with Ac_2O at 80° the reaction is Ac_2O + (I) → TlOAc + AcOH + CO.

R. T.

Inst. Organic Chem., AN SSSR

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

A

2

Structural algebra in chemistry. A. A. Malandin. *Acta Physicochim. U. R. S. S.* 13, 447-79(1940)(in English).—Theoretical-mathematical. The use of matrices to quant. chem. structural formulas is discussed. They can be applied to represent the compn., structure, configuration, movement, and orientation of mols., additive properties, equilibria, directions and velocities of reactions. "A structural matrix corresponds to a mol. and the algebraic expansion of its structural determinant corresponds to the chem. decompn. of the mol."
F. H. Rathmann

ASD-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

Ca

1

Kinetics of the thermal decomposition of nickel formate. A. A. Balandin, E. B. Grigoryan and Z. S. Yanysheva. *Acta Physicochim. U. R. S. S.* 12, 737-58(1940)(in German); *J. Gen. Chem.* (U. S. S. R.) 10, 1031-41; cf. *C. A.* 32, 3415°.—Between 215 and 270° the thermal decompn. of $Ni(OOCH)_2.2H_2O$ is complex in the initial stages because of catalysis of the decompn. reaction by the simultaneously proceeding dehydration, but obeys the equation $Ni(OOCH)_2 \rightarrow Ni + H_2 + 2CO_2$ after 60-80% decompn. The reaction is autocatalytic. At first the rate of decompn. decreases, passes through a min., then increases according to an exponential law for a reaction of $^3/_2$ order to a max. and then decreases to zero, $E = 60.1$ Cal./mol. The reaction takes place over the whole surface from the outside into the interior. K is 60% greater in air than in pure N_2. Although Ni catalysts obtained by decompn. of Ni formate in oil are catalytically active, those obtained by decompn. in air or N_2 are almost inactive. This is explained by the action of the oil in removing any CO or other sol. products formed in the initial stages during the decompn. After decompn. is complete, a slow contraction of the gaseous products takes place because of the catalytic reaction $CO + 3H_2 = CH_4 + H_2O$ with a rate of about 0.8% that of the decompn.

F. H. Rathmann

Moscow State U., Div. of Organic Catalysis of Zelinskiy Lab. for Org. Chem.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

4

Formation of 1,3-butadiene, chloroprene and acetaldehyde by the action of high-frequency electric discharge on acetylene and its mixtures with other substances. A. A. Balandin, Ya. T. Eidus and E. M. Terent'eva. *Compt. rend. acad. sci. U.R.S.S.* 27, 343-8 (1940) (in English). The reactions of C_2H_2 (I) and its mixts. with H_2, C_2H_6 and HCl in elec. discharges of high frequency were studied both in circulatory and static systems. The amt. of I converted to butadiene depended on various factors such as the diam. of the tube and electrode, kind of electrode and duration of expt., etc. Metal electrodes catalyze the reaction. The introduction of H or a compd. splitting off H_2, e. g., C_2H_6 promotes the reaction. Chloroprene and AcH were detected in the products when HCl or H_2O was added to I and the reaction carried out.

J. C. Lo Chyin

N. D. Zelinskiy Lab. Organic Chem., Moscow State U.

PROCESSES AND PROPERTIES INDEX

Ca

2

Kinetics of dehydrogenation of *sec*-butyl alcohol and reversible poisoning of copper catalysts. A. A. Balandin and A. L. Liberman. *Compt. rend. acad. sci. U. R. S. S.* 28, 794-9(1940)(in English).—To measure on the surface of Cu the mean lives of mols. of secondary alcs. and their dehydrogenation products (the ketones), and to find the true heat of activation of this reaction, expts. were made in the same manner as with primary alcs. (cf. *C. A.* 34, 6578[1]). A considerable irreversible poisoning was noticed in the dehydrogenation of *sec*-BuOH on Cu (particularly above 360°). The curves obtained for the equations showed that the activation heats of secondary alcs. are lower than those of primary alcs. 10 references.

A. H. Krappe

Inst. Organic Chem., AN SSSR, Moscow.

ASS-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

JC

A-1

Thermal decomposition of nickel formate. A. A. Balandin, [illegible] and [illegible] (J. Gen. Chem. U.S.S.R. [illegible]) —At 200° the reactions Ni + H_2 + [illegible] ← $(HCOO)_2Ni$ → Ni + H_2O + CO + CO_2 proceed simul[illegible] until about half of the formate has decomposed, after which only the former reaction persists. The activation energy of this reaction is 40·1 kg.-cal. per g.-mol., and the reaction is of the 0 order. R. T.

Moscow State Univ., Section for Organic Catalysis, Lab. of Organic Chemistry im. Acad. N.D. Zelinskiy.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

Olistal isomerism or olistomerism. A. A. Balandin. J. Gen. Chem. (U. S. S. R.) 10, 1300-1304(1940).— Parallel reactions in which the same initial substances form the same products but by different courses of reaction are defined as olistomeric reactions (from Greek word meaning glide). The conditions for these reactions are defined and discussed mathematically. A. A. P.

10

Moscow State Univ., Section of Organic Catalysis, Lab. of Organic Chemistry im. Acad. N. D. Zelinskiy.

METALLURGICAL LITERATURE CLASSIFICATION

"Reaction of Butane with Carbon Dioxide in the Presence of Catalysts," Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 1, 1941.

APPROVED FOR RELEASE: Wednesday, June 21, 2000 CIA-RDP86-00513R000103

BALANDIN, A. A.

"On the Cleav[illegible] of Non-enolizing Ketone[illegible] by Po[illegible]ium [illegible]odium Amide[illegible]," "Iz. Ak. [illegible] SSSR, Otdel. Kh[illegible]m. N[illegible]k, No. 1, 1941.

BALANDIN, A. A.

"Thermal Decomposition of Rubidium Formate," Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. [illegible],

1941.

APPROVED FOR RELEASE: Wednesday, June 21, 2000 CIA-RDP86-00513R000103

"On the Capacity of Metal Formates to be Transformed into Oxalates," Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 2, 1941.

APPROVED FOR RELEASE: Wednesday, June 21, 2000 CIA-RDP86-00513R000103

"On the Consecutive Stages of the Thermal Conversion of Formates into Oxalates," Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 2, 1941.

APPROVED FOR RELEASE: Wednesday, June 21, 2000 CIA-RDP86-00513R00010

[illegible]

"Thermal Decomposition of Cesium Formate," Iz. Ak. Nauk SSSR, Otdel, Khim. Nauk, No. 2, 1941.

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[illegible], [illegible]

"Thermal Decomposition of Lithium Formate," Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 2, 19[illegible]1.

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CA

PROCESSES AND PROPERTIES INDEX

2

Catalysis and the change of shape of molecules. A. A. Balandin. *Uspekhi Khim.* 10, [illegible](1941).—Review. Dehydrogenation leading to aromatization, selective dehydrogenation, dehydrogenation with ring closure, decyclization, mutual transformation of heterocyclic rings (furans → pyrrole or thiophene), irreversible catalysis with disproportionation, migration of double bonds, etc., are considered. The deformation of mols. and the formation of free radicals on the surface of the catalyst are discussed.
P. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA 10

PROCESSES AND PROPERTIES INDEX

Activated carbon as a catalyst in the hydrogenation of halogen derivatives by means of hydrogen. A. A. Balandin and V. V. Patrikeev. *J. Gen. Chem.* (U. S. S. R.) 11, 225-31(1941).—Pure activated C has been found to be a catalyst at 300-600° for the reaction RHal + H_2 = RH + HHal. The amt. of halogen substituted by H in the presence of activated C at 400° is as follows for the compds. investigated: PhBr, 3.0%; $CHCl_3$, 18.2%; BuBr (I), 42.0%; Me_3CCl, 81.0%; and CH_2:$CHCH_2Cl$ (II), 80.0%. Addn. of H or HCl to the double bond does not occur as is evident from the expts. with II. The Raman spectrum of I indicates that activated C causes a catalytic isomerization of the C chain. G. Berend

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CH

b

The nickel hydrides. A. A. Balandin, B. V. Erofeev, K. A. Pecherskaya and M. S. Stakhanova. *J. Gen. Chem.* (U. S. S. R.) 11, 577-80 (1941).—Ni hydrides were made under conditions described by Schlenk, Weichselfelder and Kossodo (*C. A.* 18, 207; 21, 4032). Absorption of H in an amt. exceeding considerably 4 atoms of H shows that there take place other processes which use up H: (1) soln. of H in the hydride and (2) catalytic hydrogenation of the benzene nucleus in excess of PhMgBr or in the product of the reactions $NiCl_2 + 2PhMgBr + 2H_2 = NiH_2 + 2C_6H_6 + MgBr_2 + MgCl_2$ (I) or $NiCl_2 + 2PhMgBr + 2H_2 = NiH_2 + Ph_2 + MgBr_2 + MgCl_2$ (II). The existence of I, which had been accepted by Weichselfelder, has not been confirmed. The total reaction is expressed by II. This does not, however, disprove the existence of NiH_2. PhMgBr and $C_6H_{11}MgBr$ reduce $NiCl_2$ to Ni. The colloidal Ni obtained in this manner absorbs H and forms NiH, NiH_2 and NiH_3. The existence of NiH_2 and NiH_3 was proved analytically and that of NiH kinetically. The formation of Ni hydride takes place in several stages, which are characterized by the appearance of max. and min. on the curve. These individual stages are autocatalytic; hence H dissolved in a dispersed medium reacts with colloidal Ni and with its hydrides. The reaction is completed after the absorption of 4 atoms of H per atom of Ni, with the formation of NiH_4. X-ray photographs revealed an amorphous picture, which points to an exceedingly small size of the crystals. NiH_2, NiH_3 and NiH_4 can form solid solns. with H. The stability of the solns of Ni hydrides depends on the stabilizing effect of the org. Mg compds. adsorbed on their surfaces. Twelve references.

W. R. Henn

ca

10

Styrene by catalytic dehydrogenation of ethylbenzene. A. A. Balandin, N. D. Zelinskii, G. M. Marukyan and O. K. Bogdanova. *J. Applied Chem.* (U. S. S. R.) 14, 161-72 (in French, 172) (1941).—The highest yield (of) 7?% of styrene from PhEt was obtained at 625°, an PhEt feeding velocity of 220 ml. per hr., in the presence of a V_2O_5-Al_2O_3 catalyst, and a diln. $C_8H_{10}:CO_2$ = 1:2. Lower yields of styrene were obtained in the dehydrogenation with a Cu-Al, pptd. Cu, Cu with Cr_2O_3 promoter, without and with diluents such as N and CO_2 (under different conditions). A detailed description of the procedure is presented. 14 references. A. A. B.

CA

PROCESSES AND PROPERTIES INDEX

2

Stages in heterogeneous catalysis. Dehydrogenation reactions.—A. A. [illegible].—*Acta Physicochim. U. R. S. S.* 14, [illegible]-44(1941); cf. *C. A.* 36, [illegible].—A theoretical discussion, chiefly from the point of view of the multiplet theory (*C. A.* [illegible]). A reply to Taylor's criticism (*C. A.* 35, [illegible]) is included.
B. C. P. A.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

10

Preparation of bivinyl by catalytic dehydrogenation of butene. A. A. Balandin, N. D. Zelinskii, O. K. Bogdanova and A. P. Shcheglova. *J. Applied Chem.* (U.S.S.R.) 14, 435–45 (in French, 445) (1941); translation in *Foreign Petroleum Tech.* 9, 285–92 (1941). — The reaction was carried out in the presence of the following catalysts: Cr_2O_3, Cr_2O_3 on kieselguhr (25% by wt.), Cr_2O_3 and 20% of a mineral closely related to zircon, Cr_2O_3 and CuO (10%), Cr_2O_3 and ZnO (0.1% by wt.), Cr_2O_3 and MoO_3 (50 mol. %), V_2O_5 and Al_2O_3 (20.4% by wt. of V_2O_5), the same obtained by joint pptn., Ag_3VO_4 (33% by wt.) on kieselguhr (67% by wt.), MgO, and Cr_2O_3 prepd. in a special way. The reaction was carried out at atm. pressure while contacting for 0.3 sec. and passing butene in a mixt. with CO_2 (ratio 1:7.5% by vol.). At 600° the bivinyl yield amounts to 24% on the passed and 77% on the decompd. butene, while at 550° the yield on the passed butene is 27% and on that decompd. 82%, requiring then 3 hrs. The other products of reaction are H_2 and CO in equimol. proportions with a slight admixt. of C_2H_4 and satd. hydrocarbons. 10 references. A. A. Boehtlingk

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

PROCESSES AND PROPERTIES INDEX

Theory of complex reactions. I. Foundations of the theory. Kinetic simplexes. A. A. Balandin. *J. Phys. Chem.* (U. S. S. R.) 15, 615-28(1941).—An introduction to a math. theory of complex reactions is presented. By means of structural algebra an analogy is drawn between the methods of linking of atoms in a mol. and that of linking of simple elementary reactions into complex reactions. Two types of graphic representation of complex reactions are presented: the use of kinetic formulas structurally corresponding to the formulas of mol. structure and the use of kinetic figures principally corresponding to the stereochemical models. Both types are closely linked with structural matrices. It is shown that the law of the interacting masses for complex reactions can be expressed in the same form as that for the simple reactions if the magnitudes used in the expression for simple reactions are considered as definite structural matrices. The kinetic elements, simple reaction components of the complex reactions, are discussed and an analogy is traced between them and the atoms and radicals of chem. compds., including the principle of valence. Topologically, they are simplexes of a special type, which are shown to have isomeric forms. II. Kinetic complexes. Diagrams of properties. Superreactions. *Ibid.* 629-44.—The combination of the kinetic simplexes into complexes is considered. Isomerism in the representation of complex reactions is much more developed than it is for mol. structures. Isomerism and classification of bi-tertiary reaction complexes is presented. Kinetic formulas and kinetic diagrams are applied to available exptl. material on kinetics of complex reactions. It is shown that the equil. diagrams of physicochem. analysis are projections of the kinetic diagrams; the former (compn.-properties of chem. systems) are included in the analogy between mols. and the complex reactions, being analogs of atoms and radicals. This analysis is carried through to "superreactions," i. e., interaction of reactions. The theory is presented in the form of structural algebra.

G. M. Kosolapoff

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ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

Ca

PROCESSES AND PROPERTIES INDEX

10

Catalytic dehydrogenation of butylene to butadiene. A. A. Balandin, N. D. Zelinskii, O. K. Bogdanova, and A. P. Shcheglova. *Kauchuk i Rezina* 15, No. 4, 4-7 (1941); cf. *C.A.* 37, 2335[9].—Dehydrogenation of α-butylene over a Cr catalyst in a previously used app.

(*C.A.* 36, 2254[9]), using normal pressure, 575°, and 0.35-sec. contact, showed a butadiene yield of 7.4 mol.-% per pass (46.7% of decompd. butylene); under the same conditions but with the pressure reduced to 510 mm., the yield was 8.8% (83.0%); under the same conditions but with a 1.5-sec. contact, the yield was 12.0% (41.0%). The yields were much higher at 600° and reduced pressures, being 28% (87.5%) at 600°, 100 mm. pressure, and 0.70-sec contact. Reduced pressures and temps. below 600° resulted in lower yields. The gaseous products consisted mostly of about equal amts. of butadiene and H and also unreacted butylene.

B. Z. Kamich

METALLURGICAL LITERATURE CLASSIFICATION

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CA

Catalytic dehydrogenation of cyclopentane in the presence of chromic oxide. A. A. Balandin and V. E. Fedorov. *Compt. rend. acad. sci. U. R. S. S.* 30, 21-2(1941)(in English).—Upon heating with Cr_2O_3, cyclopentane is dehydrogenated to the extent of 3.8% at 370°, 4.4% at 410° and 6.1% at 470°. These results are comparable with those obtained for cyclohexane under the same conditions (cf. *C. A.* 31, 600°), thereby supporting the edge mechanism of the reaction.

J. H. Reedy

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ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

BALANDIN, A. A.

Catalytic dehydrogenation of n-butane. A. A. Balandin, N. D. Zelinski, M. N. Marushkin, and L. N. Pavlov (Compt. rend. Acad. Sci. U.S.S.R., 1941, 32, 135-138).--The yields of butenes, C_4H_8, H_2 and saturated hydrocarbons obtained from n-C_4H_{10} with a mixed Cr catalyst at 525-625° and times of contact 0·8--3·5 sec. are recorded. The yield of butenes is 95% (based on C_4H_{10} decomposed) at 550-575° after contact for 2 sec. The catalyst is deactivated by cooling in N_2 and reactivated by heating in air.

Inst. Org. Chem., AN SSSR

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A L-F

PROCESSES AND PROPERTIES INDEX

Chemistry and structure. IV. Application of determinants of structure matrices to solution of the equation with isomorphously substituted matrices. A. A. Balandin (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1942, 256–260). Determinants with isomorphously substituted matrices can be applied to the analysis of fraction systems of simultaneous and consecutive reversible first order stages. If the determinant $|B| = 0$, where B is the substituted matrix, the algebraic sum of all the velocity coeffs. of the system is zero.

E. A. B.

Inst. Organic Chem., AN SSSR

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

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Preparation of butadiene for the synthesis of rubber by catalytic dehydrogenation of butylenes at reduced pressure. A. A. Balandin, N. D. Zelinskii, O. K. Bogdanova and A. P. Shcheglova. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1942, 319-20 (English summary); cf. C.A. 37, 2339.—With a Cr catalyst at 180 mm. pressure, on rise of temp. the max. dehydrogenation is effected in shorter contact time. The temp. coeff. of decompn. is higher than that of dehydrogenation; hence at higher temps. decompn. losses increase. At approx. optimum conditions (180 mm. pressure, 600° and 0.78 sec. contact) 28.0 mol. % butadiene was obtained, based on the butylene inflow. Rates of dehydrogenation of the 2 forms of butylene are approx. the same. C deposition on the catalyst shows the normal increases with rise of temp.

O. M. Kosolapoff

"The Catalytic Dehydrogenization of Hydrocarbon And Its Application To The Synthesis of Rubber from Gases," Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 1, 1942. Acad. Sci. of the USSR. Institute of organic Chemistry. Department of N. D. Zelinsky, member of the Academy. - 1942-.

BALANDIN, A. A.

"Kinetics of catalytic monomolecular reactions in a flow system taking into consideration the displacement with foreign substances." (p. 159)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1942, Vol 12, No 3-4.

Inst. Organic Chem., AN SSSR

BALANDIN, A. A.

"On reaction-kinetical method of determination of anisochrony." (p. 167)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1942, Vol 12, No 3-4.

Inst. Organic Chem., AN SSSR

BALANDIN, A. A.

"Topochemical factors in the formation of the hydrides of nickel." Balandin, A. A., and Erofeew, B. V. (p. 170)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1942, Vol 12, No 3-4.

Inst. Org. Chem., AN SSSR

BALANDIN, A. A.

"The kinetics of the interaction of sodium acetate and sodium hydroxyde in the molten state." Balandin, A. A., Jurba, L. I., and Waskevitsch, D. N. (p. 179)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1942, Vol 12, No 3-4.

Inst. Organic Chemistry, AN SSSR

BALANDIN, A. A.

"The selective effect of nickel catalyst and the energy of chemical linkages." (p. 342)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii) 1942, Vol 12, No 7-8.

Inst. Org. Chem., AN SSSR

BALANDIN, A. A.

Catalytic dehydrogenation of butylene to butadiene at reduced pressure. A. A. Balandin, N. D. Zelinski, O. K. Bogdanova, and A. P. Schtscheglova (J.Appl.Chem.Russ.,1942,15,128-138).----- Δ-Butene (I) passed through an unspecified catalyst gives buta-diene; the yield is up to 85% on the (I) consumed and up to 29% on the (I) passed through; the best temp. is 580-600°. The yield of $(CH_2CH)_2$ is almost independent of the rate of gas flow and nearly as high as corresponds to the equilibrium concn. A few % of (I) are isomerised to Δ-butene, and a few % are formed.

J. J. B.

BALANDIN, A. A.

Dehydrogenation and decomposition of cyclohexane at high temperatures over metallic catalysts. A. A. Balandin and N. Z. Kozelkov (J.Appl.Chem.Russ.,1942,15,139-150).--cycloHexane (I) was passed over heated metal spirals. There was no decomp. with Fe below 550° or with Cr-plated Fe below 500°; a little decomp. occurred with nichrome at 300°, and at higher temp. much CH_4 etc. was formed in addition to C_6H_6. Platinised nichrome dehydrogenates (I) at 300-400°; the rate is lowered by dilution with CO_2 at 300-350° and raised by dilution with N_2 at 400°. Soot gradually builds up on the catalyst, and the energy of activation drops from 10kg.-cal. to 5 kg.-cal.per mol.; the activity of the catalyst has a max. at some medium soot content. An explanation is given for the promoter effect of soot. Palladised nichrome is less active than platinised nichrome, and the energy of activation (without soot) is 7 kg.-cal.

BALANDIN, A.

"Sliding" isomerism ("olisthomerism"). A. Balandin (Acta Physicochem. URSS., 1942, 16, 195-205). --Where it is possible by change of groups in different ways to arrive at the same compound from the same starting materials, the products are called "sliding" isomerides or olisthomerides. Thus, in the formation of MeOAc from AcOH and MeOH, the substances may combine as follows: Me OH + MeCO OH and Me OH + MeCO O H. Conditions for the existence of this type of reaction are outlined. Reactions in which it may take place include esterification, formation of ethers from alcohols, formation of mixed acid anhydrides, mixed ketones, aldehydes from formic and another carboxylic acid, (sec.) amines from two primary amines, and the reaction between two different peroxides, etc. The investigation of the reactions provides an important method for comparing the strengths of linkings and the mobility of groups and atoms. Isotopes, artificial radioactivity, and optical activity can also be introduced into the study of the phenomenon. A.J.M.

State U.,
Div. of Organic Catalysis of the Zelinskiy Lab., Moscow.

Kinetic study on the dehydrogenation of cyclohexane. A. A. Balandin and F. L. Kostin (*Acta Physicochim. U.R.S.S.*, 1942, 17, 311—317).—The catalytic dehydrogenation of cyclohexane was investigated at 380—530° with Cu on Cr_2O_3 (I), Cu on Cr_2O_3 with BaO (II), and Cr_2O_3, from $Cr_2(CrO_4)_3$ (III) as catalysts. C_6H_6 is the main product, the yields at 530° being 100% with (I), 13% with (II), and 81% with (III). Contrary to usual results, catalyst (III) did not lose its activity after 80 hr. in use. With increasing temp. the yield of unsaturated hydrocarbons obtained with (III) decreased. Determination of the activation energy and the pre-exponential factor for the reaction show that the sextet mechanism proposed previously (A., 1937, I, 90) is operative for reaction on catalyst (I); in the other cases the duplet mechanism occurs. J. F. H.

Moscow State U.

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Differential equation for the kinetics of contact unimolecular reactions investigated by the flow method. A. A. Balandin (Acta Physicochim. U.R.S.S., 1942, 17, 213-223). - Theoretical. The results are applied to the dehydrogenation of alcohols and to contact isomerisation. J. W.

Inst. Organic Chem., AN SSSR

PROCESSES AND PROPERTIES INDEX

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Catalysis of dehydrogenation and decomposition of cyclohexane and the dendrite hypothesis of deposition of C. A. A. Balandin and N. Z. Kotelkov. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1943, 130-1.—Cyclohexane was passed over Pt, Pd and Ni catalysts at 300-600°. On platinized nichrome cyclohexane is only dehydrogenated to 600°; at 800° complete decompn. to C, H and CH_4 occurs. Pd-nichrome causes some dehydrogenation at 400°, but nichrome alone is weakly active at 400°. Fe is not active to 800°. Deposition of C to a certain extent fails to diminish the dehydrogenation reaction. The results are consistent with the dendrite hypothesis.

G. M. Kosolapoff

A.S.M.-S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

Carbon deposition in the decomposition of ethylbenzene on metal surfaces and the study of this process by means of a photoelement. A. A. Balandin and V. V. Patrikeev (*Compt. rend. Acad. Sci. U.R.S.S.* 1942, 36, 88—92).—C deposition occurring in high-temp. catalytic processes is studied by following the decrease in the amount of light reflected on to a photo-electric cell from a highly polished metal surface held in the reaction chamber. The method has been applied to the study of the catalytic decomp. of PhEt in presence and in absence of unsaturated hydrocarbons. The reaction has an induction period which decreases with rise of temp. from 480° to 680°; the rate of C formation also increases with temp. J. L. R.

Inst. Organic Chem., AN SSSR

Preferential paths in contact catalysis. A. A. Balandin (*Acta Physicochim. U.R.S.S.*, 1942, 17, 73—81).—Calculations of the probabilities of reactions on Ni catalysts based on the multiplet theory (cf. A., 1939, 519; 1941, I, 341) are revised, using new bond strength data. The results (in general unchanged by the new data) agree with experiment. Several new reactions are considered on this basis. J. H. Ba.

Inst. Organic Chem., AN SSSR

APPROVED FOR RELEASE: Wednesday, June 21, 2000 CIA-RDP86-00513R00010

BALANDIN, A. A.

Contact decomposition of hydrocarbons. Conversion of n-butane under the action of carbon dioxide over nickel-alumina catalysts. A. A. Balandin, M. N. Maruschkin, and M. M. Afanasiev (*Acta Physicochim. U.R.S.S.*, 1942, 17, 83—92).—With rise in temp. (θ) from 400° to 800°, [CO] and [H_2] of the product from C_4H_{10} and CO_2 over a Ni–Al_2O_3 catalyst increase, and the vol. increases ten-fold. The hydrocarbon content is all CH_4 at 800° (amount decreasing with θ). For low initial CO_2 content, CH_4 is > original C_4H_{10}, indicating decomp. of C_4H_{10}, and decrease in the C and H content of products indicates decomp. to C. C_2H_6 is found in some experiments but is not due to pyrolysis since no olefines are produced. The results are explained on the multiplet theory (cf. preceding abstract). With the catalyst the C_4H_{10} first suffers rupture of a primary C–H linking followed by that of C–C to give H, CH_3, and Pr. Pr and H recombine to give C_3H_8, and CH_3 with CO_2 gives CO and H_2. The shortened chain repeats the process (calculation shows it to be more favourable). Alternatively CH_3 gives C and H_2 or is hydrogenated to CH_4. CO_2 and PrCHO under similar conditions give olefines (amount increases with θ) as well as paraffins but θ must be higher than with C_4H_{10}. This indicates that PrCHO is not an intermediate in the C_4H_{10}–CO_2 reaction. J. H. Ba.

Inst. Organic Chem., AN SSSR

PROCESSES AND PROPERTIES INDEX

C 4

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Chemistry and structure. V. The properties of structure determinants. Expansion of structure determinants. A. A. Balandin. *Bull. acad. sci. U. R. S. S., Classe sci. chim.* 1943, 30–42 (English summary); cf. *Ibid.* 1942, 285; *C. A.* 39, 3804[9].—Theorems in structural algebra are developed and math. proof is given of the usefulness of structure determinants in detg. chem. structure as proposed by B. (*C. A.* 36, 7071[9]) H. M. Leicester

Inst. Organic Chem., AN SSSR

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

Al 8, Reactions

Thermal study of catalytic reactions by means of the differential thermocouple. A. A. Balandin and V. V. Patrikeev (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1943, 470–477).—Information as to the course of a catalytic reaction may be obtained by a thermocouple, one junction of which is in the catalyst and the other in similar, but inert, material placed adjacent to it. V. R.

PROCESSES AND PROPERTIES INDEX

Selective hydrogenation. A. A. Balandin (*Bull. Acad. Sci. U.R.S.S., Cl. Sci. Chim.*, 1942, 477—478).—An equation of a general type is deduced whereby velocity-time curves for hydrogenation reactions can be calc. (see following abstract). V. B.

ASO-SLA METALLURGICAL LITERATURE CLASSIFICATION

3e

A/

Spatial arrangement of atoms in contact catalysis and dehydrogenation of hydrocarbons with open chains. A. A. Balandin (*Acta Physicochim. U.R.S.S.*, 1943, **18**, 60—60).—The multiplet theory of catalysis, in which the shape and size of mols. and of the lattice of the catalyst are regarded as of primary importance, is discussed with particular reference to the dehydrogenation of hydrocarbons. Models indicating the orientation of n-C_4H_{10} (I), Δ^{α}-butene (II), and PhEt mols. when undergoing catalytic dehydrogenation are drawn, and the reactions are studied, using the flow method. With (I), the dehydrogenation at a Cr_2O_3 catalyst amounts to 83% of (I) passed, or to 88% of that decomposed at 670°, and a spatial velocity of 700—1000 l. per hr. At lower temp. the yield on the basis of (I) passed decreases, [illegible] based on (I) decomposed increases. The yield-t[illegible] curves, drawn for various temp., show a max. [illegible] t. The composition of the contact gas [illegible] H_2 37·8%, CH_4 2·4%, C_2H_6 3·7%, [illegible] C_4H_8 30%, C_4H_{10} 20·8%. The dehydr[illegible] of C [illegible] with one another on Cr_2O_3 c[illegible] and the Cr_2O_3 [illegible] deactivated owing to C films, but is readily regenerated. With (II), activity decreases above a certain temp., probably owing to decomp. of products. The yield of butadiene at 600° is 34% based on (II) passed and 78% based on (II) decomposed. The most important side-reaction is $C_4H_8 + 4CO_2 = 8CO + 4H_2$, but the CO does not poison the catalyst. The activity varies with time in a peculiar manner. The dehydrogenation of (II) has also been investigated at low pressures, in which case the optimum *t* is greater. The effect of dilution with CO_2 and N_2 was also studied. Two methods for the production of styrene (III) from PhEt are given. There is again an optimum *t*. The effect of addition of (III), PhMe, and C_6H_6, respectively, to PhEt undergoing dehydrogenation indicates the following sequence of mean lives of mols. on the active surface: (III) > PhEt > PhMe > C_6H_6. The curves of yield of (III) against *t* are similar to those obtained in the pyrolysis of PhEt.

A. J. M.

Inst. Organic Chem, AN SSSR

IIA

L

Composition and mechanism of formation of the hydrides of Ni. I. Composition of the hydrides of Ni. A. A. Balandin, B. V. Erofeev, K. A. Pecherskaya and M. S. Strakhova. *Acta Physicochimica U. R. S. S.* 18, 157-166 (1943)(in English); cf. *C. A.* 37, 2673[5]. Under the exptl. conditions described by Schlenck, *et al.* (*C. A.* 18, 207) the hydride of Ni formed has the compn. NiH_2 rather than NiH_3. NiH_2 was prepd. by interaction of $NiCl_2$, H gas, and C_6H_5MgBr dissolved in Et_2O, Bu_2O, C_6H_6, toluene or xylene in a H atm. It was analyzed by thermal decompn. to Ni and H_2. NiH_2 is formed as an intermediate product and strongly catalyzes the hydrogenation of C_6H_6 and ylene F. H. Rathmann

Inst. Organic Chem., AN SSSR

Composition and mechanism of formation of the hydrides of nickel. II. Reaction mechanism. A. A. Balandin, B. V. Jerofeev, K. A. Pecherskaja, and M. S. Stachanova (*Acta Physicochim. U.R.S.S.*, 1943, 18, 300–310). Weichselfelder's view that the formation of NiH_2 from $NiCl_2$, MgPhBr, and H_2 is due to the interaction of H_2 with $NiPh_2$, formed as an intermediate compound, is incorrect. $NiCl_2$ is reduced to Ni by MgPhBr in absence of H_2. The formation of Ni hydrides by interaction of reduced Ni and H_2 proceeds in stages. These stages are autocatalytic, the dissolved H_2 reacting with solid Ni and with the hydrides and NiH, NiH_2, and NiH_4 are formed. The Ni surface is poisoned by certain strongly adsorbed compounds, *e.g.*, thiophen, which prevent the penetration of H_2 to the Ni surface and formation of hydride. The poisoning effect is even greater for catalytic hydrogenation of the C_6H_6 nucleus, on the other hand, the poisoning effect on the dissolution of H_2 in the hydrides is very small. Sols of Ni hydrides in Et_2O and other solvents were examined. Those in Et_2O are less stable than those in C_6H_6, PhMe, and xylene. Colloidal solutions in Et_2O are formed only when [MgPhBr] is >0·5M, suggesting that adsorption of MgPhBr on the hydride surface protects the colloid. H_2O and air rapidly coagulate the sols. C. R. H.

Dendrite hypothesis of carbon deposition. Chemical behaviour of cyclohexane when in contact with electrically heated metallic coils. A. Balandin and N. Kotelkov (*Acta Physicochim. U.R.S.S.*, 1943, 18, 408—419).—The catalytic dehydrogenation and decomp. of cyclohexane over Pt- and Ni-nichrome, nichrome, Cr-Fe, and Fe at 300—600° has been investigated. Nichrome, Cr-Fe, and Fe are inactive. Ni-nichrome is a poor catalyst. Pt-nichrome is a good catalyst at higher temp. The deposition of C does not diminish the dehydrogenation activity of the catalyst; on the contrary, the activity is increased. Deposition of C in the form of dendrites is suggested in explanation.

C. R. H.

Moscow State U.;
Inst. of Organic Chem., AN SSSR.

BC

A-1

Progressive poisoning of hydrogen sorption in the process of formation of nickel hydrides. A. A. Balandin and B. V. Jerofeev (*Acta Physicochem. U.R.S.S.*, 1943, 18, 494—496).—Discussion of data on the formation of Ni hydrides (cf. A., 1944, I, 183, 286) leads to the view that three kinds of reaction sites with different adsorption potentials exist on the Ni surface. The sites with the highest potential condition catalytic hydrogenation of the org. liquid medium, those with intermediate potential condition Ni hydride formation, and those with the lowest potential condition dissolution of H_2 in the hydrides. The poisoning is progressive, the reaction at a given site depending on the adsorption potential at the moment.
C. R. H.

Inst. Organic Chem., AN SSSR

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

F

922. FORMATION OF OLEFINES FROM HIGH PARAFFINIC HYDROCARBONS. Balandin A A and Marushkin M N (Compt. rend. acad. sci. U.R.S.S. 30/3/1943, 40, 226; B.C.U.R.A. Bull.) Paraffin wax (m.p. 50° C., av. mol. wt. 554) was passed as vapour over a chromium oxide catalyst at 450° 550° C. The products had lower molecular weights (285-450) and contained 30%-60% unsaturateds. Some decomposition occurred, with formation of carbon, methane and hydrogen. A little aromatisation also occurred.

ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION

Kinetics of consecutive reactions consisting of bimolecular and unimolecular stages. A. A. Balandin and L. S. Leibenson (Compt. rend. Acad. Sci. U. R. S. S., 1943, 39, 22-24).--The equations for consecutive reactions of the type $2A \rightarrow B \rightarrow C$ are solved, and the results compared with experiment in the case of the formation of CH_4 from equimol. mixtures of NaOAc and NaOH. The reaction is made up of two consecutive ones. The first, the formation of an intermediate compound, is bimol., and has a velocity coeff. $\ll$ that of the unimol. conversion of the intermediate compound into the final products. The concn. of the intermediate compound is small.

A. J. .

Inst. Organic Chem., AN SSSR.

Formation of C dendrites by catalytic decomposition of [illegible]. A. A. [illegible] and V. V. Patrikeev. Doklady [illegible] 171-4 (1943); Compt. rend. [illegible] (in English); cf. C.A. [illegible] —Soot dendrites were formed on a [illegible] wire when iso-PrOH was passed over it at 480°. The dendrites, having an empirical formula [illegible], probably are built up of cryst. layers of 6-member C rings arranged in the graphite lattice, with the H atoms attached to the C atoms of the periphery. No dendrites were formed when CO_2 was mixed with the iso-PrOH before passing it over the hot wire. J. W. Perry

Inst. Organic Chem., AN SSSR.

METALLURGICAL LITERATURE CLASSIFICATION

CA

PROCESSES AND PROPERTIES INDEX

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Formation of olefins from higher paraffinic hydrocarbons. A. A. Balandin and M. N. Marushkin. *Doklady Akad. Nauk S.S.S.R.* 40, 284-7(1943); *Compt. rend. acad. sci. U.R.S.S.* 40, 258-9(1943)(in English).—Solid paraffin (m. 50°, av. mol. wt. 384) was exposed, at temps. of 450–550°, to the action of a dehydrogenating catalyst contg. Cr (cf. *C. A.* 37, 867). Tabulated analyses of the reaction products indicate that 4 different reactions occurred, viz. (I) dehydrogenation to form olefins without cracking, (II) formation of aromatic compds. without cracking but with splitting off of H, (III) simple fission to form olefins and satd. hydrocarbons, (IV) complete cracking to CH_4, C and H_2. The extent of these reactions was as follows: at 450°, I 30%, II 8%, III 20%, IV 4%; at 500° I 30%, III 21%, IV 5%. At 550°, the total yield of olefins was larger yet, but cracking also increased as indicated by the liquid character of the condensate and by the halving of the latter's av. mol. wt.

J. W. Perry

Inst. Orgamic Chem., AN SSSR

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

Ca

10

Catalytic dehydrogenation of p-cymene. A. A. Balandin, G. M. Marukyan and R. G. Seimovich. *Doklady Akad. Nauk S. S. S. R.* 41, 71-3(1943); *Compt. rend. acad. sci. U. R. S. S.* 41, 67-9(1943)(in English).—Conversion of p-cymene (I) into α,4-dimethylstyrene (II) can be carried out efficiently by using catalysts and conditions previously worked out for conversion of EtPh into styrene (cf. *C. A.* 36, 417[7]). Optimum conversion of I into II amounted to 63.4% when 2 mols. CO_2 were admixed per mol. I before passing over the catalyst, which retained its activity after use for 81 hrs. Without CO_2, the best conversion of I was 38.3%. Supplementary expts. showed that II can be polymerized by heat, cold, concd. H_2SO_4 or $SnCl_4$.

J. W. Perry

Cor. Mbr., AN SSSR

Inst. Org. Chem., AN SSSR

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

ca

2

Kinetics of hydrogenation of unsaturated and aromatic hydrocarbons. A. A. Balandin. *Bull. acad. sci. U.R.S.S., Classe sci. chim.* 1944, [illegible]-60.—A theoretical and mathematical discussion of the applicability of the general kinetic equation of hydrogenation of hydrocarbons to special cases of hydrogenation over Ni and over Pt at high and at low temps., with possible simplifications of the general equation. Hydrogenation of C_6H_6 over Cu at low temp and low pressure is briefly discussed. G. M. K.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

CA

2

Differential thermocouple in heterogeneous catalysis. A. A. Balandin and V. V. Patrikeev. *J. Gen. Chem. (U. S. S. R.)* 14, 87-90(1944)(English summary).—A description of app. and procedure for the use of differential-thermocouple installations for the study of heterogeneous catalysts and catalytic processes in flow systems with the use of automatic continuous recording of temps. The procedure is applicable in a wide variety of studies of comparison of catalyst activities, detn. of relative activity vs. time, detn. of thermal data of the reactions. When alcs. are passed over Al_2O_3 in a CO_2 atm. there exists a brief exothermic effect that has not been reported heretofore.

O. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

Lab. Kinetic Contact Org. Reaction, Inst. Organic Chemistry, AN SSSR

M

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Ca

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Dehydrogenation of EtOH over mixed catalysts. S. L. Lel'chuk, A. A. Balandin, D. N. Vaskevich and I. I. Greer. *J. Applied Chem.* (U. S. S. R.) 17, 60-4(1944) (English summary).—Using 3-component catalysts of Cu-Al_2O_3 promoted by Cd or Tl oxides EtOH was dehydrogenated with the formation of considerable amts. of AcOH and EtOAc. The Cd-promoted catalyst has no advantage over the Cu-Al_2O_3 catalyst, while TlO_2 promoter favors the EtOAc formation: at 300 cc. per l. catalyst volume-rate at 285° there may be obtained per pass up to 33.7% EtOAc and 19% AcOH. The formation of EtOAc on the TlO_2-promoted catalyst has a lower activation energy (9770 cal./mol.) than on the Cd oxide-promoted catalyst (14,800 cal./mol.). O. M. Kosolapoff

Allylic rearrangements. XVI. The addition of the butenyl Grignard reagent to some simple carbonyl compounds. John D. Roberts and Wm. G. Young. *J. Am. Chem. Soc.* 67, 148-50(1945); cf. *C. A.* 39, 2060.—Butenylmagnesium bromide (I) (Part XV) and HCHO in ether give octadienes (b. 65-108°) and 80% of 2-methyl-3-buten-1-ol (II), b. 120-1°, n_D^{20} 1.4261; *3,5-dinitrobenzoate*, m. 87.5-8°; the structure of II follows from the action of O_3, which gives HCHO, and reduction to 2-methyl-1-butanol. I and Me_2CO give 81% of *2,3-dimethyl-4-penten-2-ol*, b. 94.5-4.9°, n_D^{20} 1.4308; *3,5-dinitrobenzoate*, m. 78-9.5°. I and AcH give 84% of *3-methyl-4-penten-2-ol*, b. 120-8°, n_D^{20} 1.4315; *3,5-dinitrobenzoate*, m. 44-5.5°; hydrogenation gives 3-methyl-2-pentanol; not more than 5% of the total product could have been 4-hexen-2-ol. The products result from the secondary form of I (RCH(MgX)CH:CH_2) and not RCH:CHCH_2MgX. Carbonation of the Grignard reagent from CH_2:CHCH(OH)Me gives 70% of CH_2:CH·CHMeCO_2H; dibutenylmagnesium gives 37% of the same acid. Thus, the equil. in the Grignard soln. of the type $2RMgX \rightleftharpoons R_2Mg + MgX_2$ appear to have no effect on the final products from addn. to C=O double bonds where no great quantity of steric hindrance may be expected. C. J. West

ASA-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Anisochronism and its experimental determination. A. A. Balandin. *Acta Physicochim. U.R.S.S.* 19, 312-22(1944)(in English).—Math. and theoretical. The anisochronism of the substances *A* and *B* is defined as a quantity that shows, as a ratio, how much longer a mol. of *A* remains in the adsorbed state on the active surface of a catalyst than does a mol. of *B*. On the basis of equations developed previously (*C.A.* 37, 4612) 2 methods, one simplified and one exact, are developed for detg. the mean lifetimes of mols. on the active surface and hence for detg. the anisochronism. These methods involve measuring reaction kinetics (1) with the pure reactant at different low pressures and (2) with mixts. of the reactant and the substance to be tested at const. (atm.) pressure. It is unnecessary to work with mixts. under diminished pressure to det. the mean lifetimes and the anisochronism.

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

"The Differential Thermocouple Method in Contact Catalysis." Acta Phys., Vol. XIX, No. 6, 1944. Acad. of Sci. of the USSR, Inst. of Organic Chem., Moscow.

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p,α-Dimethylstyrene. A. A. Balandin, G. M. Marukyan and R. G. Schmovich. U.S.S.R. 64,222, Jan. 31, 1945. *p*-Cymene is catalytically dehydrogenated in the vapor phase at 600°, at ordinary or reduced partial pressure of the *p*-cymene. Partial pressure of the cymene can be reduced either by diln. with CO_2 or by employing a vacuum.

M. Hosch