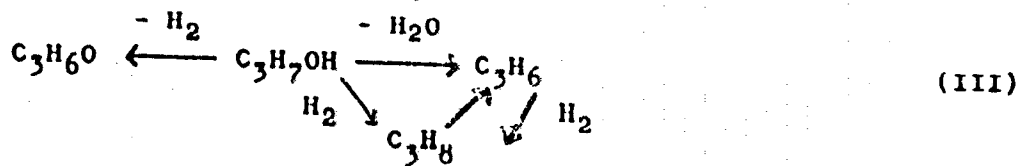


33491

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:



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.

Card 4/5

33491

The use of radiocarbon (C^{14})

S/195/61/002/003/016/027
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)

✓

Card 5/5

33492

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

11.0132

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),
Card 1/3

Investigation of the role of

33492

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

E030/E185

benzol, and marked cyclohexene (activity 470 pulses/minute mg BaCO₃) obtained from C¹⁴ 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

Card 2/3

X

33492

Investigation of the role of

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

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:

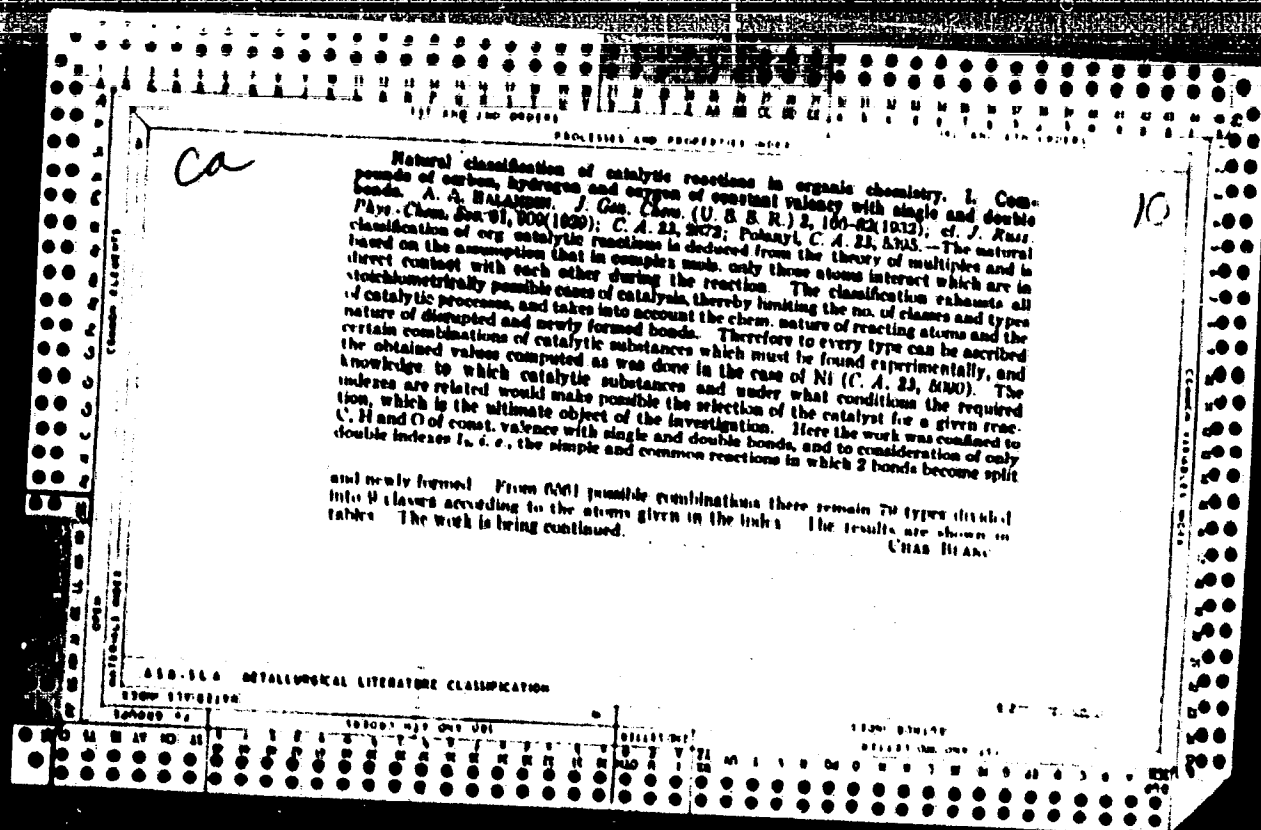
- Ref. 3: H.H. Long, J.C.W. Frazer, E. Ott,
J.Amer.Chem.Soc., v.56, 1101, 1934.
- Ref. 4: P.H. Emmett, N. Skau,
J.Amer.Chem.Soc., v.65, 1029, 1943.
- Ref. 11: H.S. Taylor, J.Amer.Chem.Soc., v.60, 627, 1938.
- Ref. 13: E.F.G. Herington, E.K. Rideal,
Proc.Roy.Soc., London, v.A190, 289, 1947.

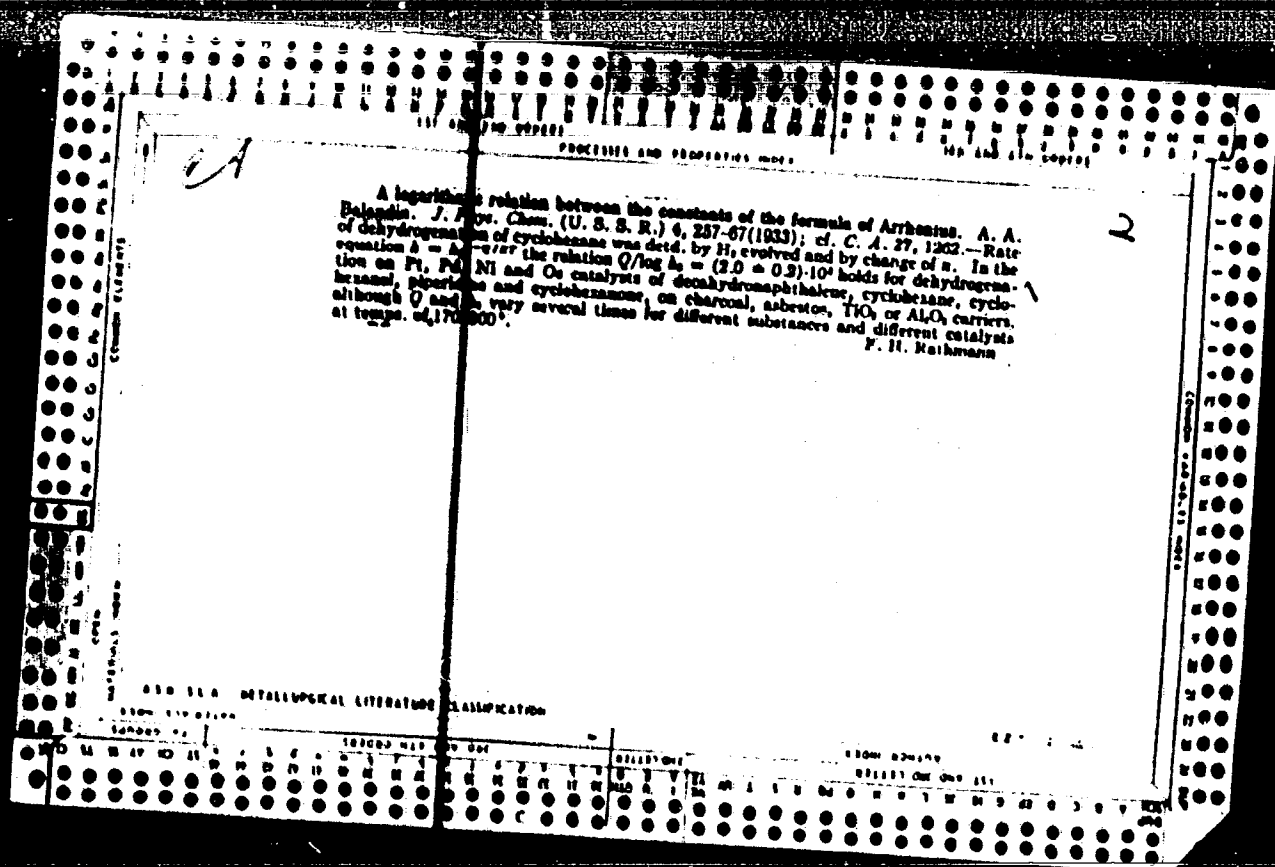
ASSOCIATION: Institut organicheskoy khimii im. N.D. Zelinskogo
AN SSSR
(Institute of Organic Chemistry imeni
N.D. Zelinskiy, AS USSR)

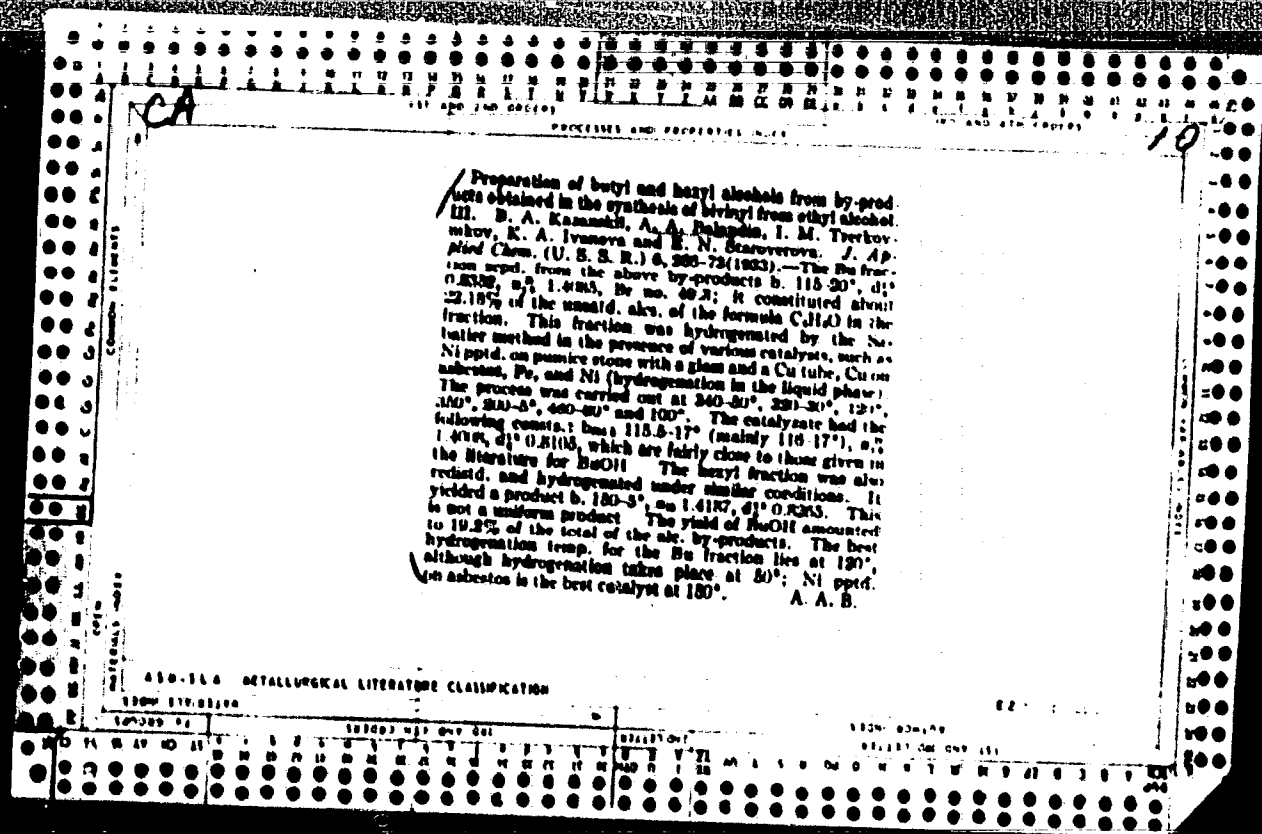
Card 3/3

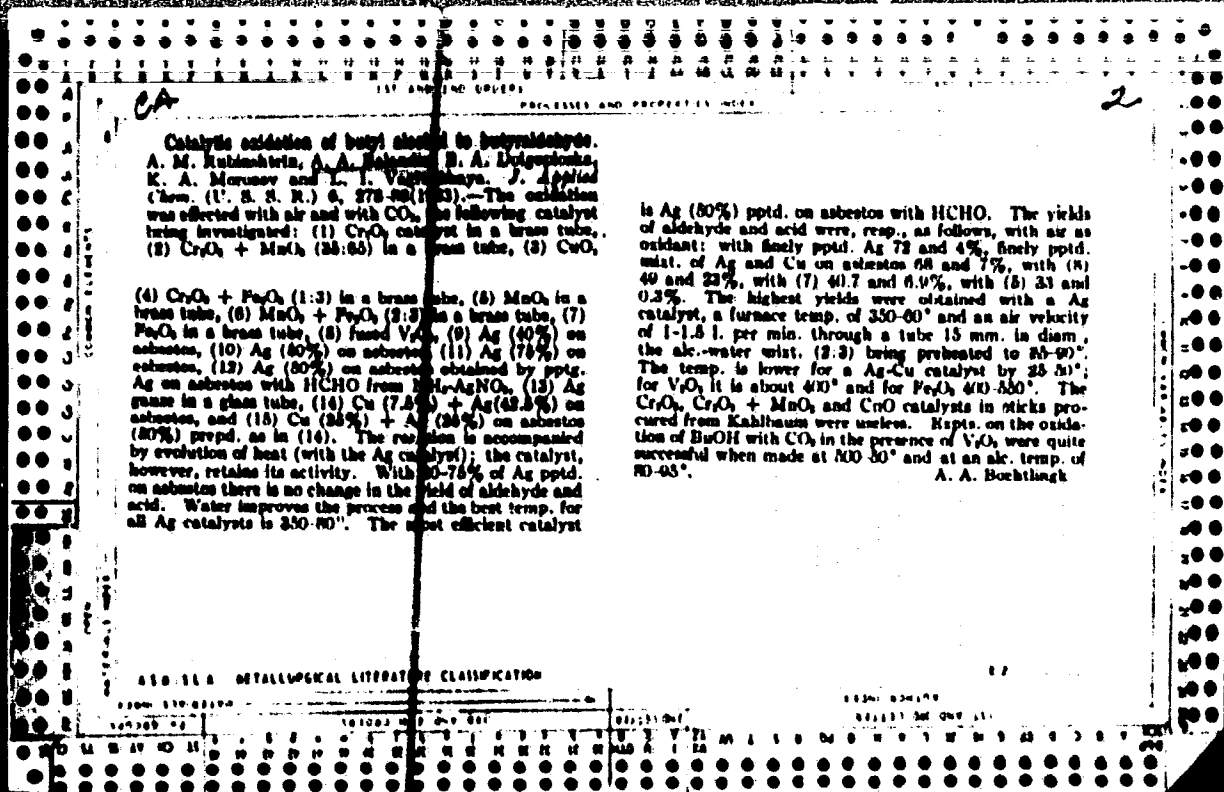
Decomposition reactions in the process of catalytic hydrogenation in presence of nickel. Role of the catalyst in heterogeneous catalysis. A.A. Balandin (J. Russ. Phys. Chem. Soc., 1930, 62, 703-728). - An empirical rule is given, the use of which allows the products of catalytic hydrogen of organic substances to be predicted. If the values 1, 2, 3, and 4 be assigned to the 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 hydrogenation 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 above four elements for a series expressing facility of replacement of the given element from its compound with nickel by a different element in combination 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 catalyst need not be the same as in its presence.

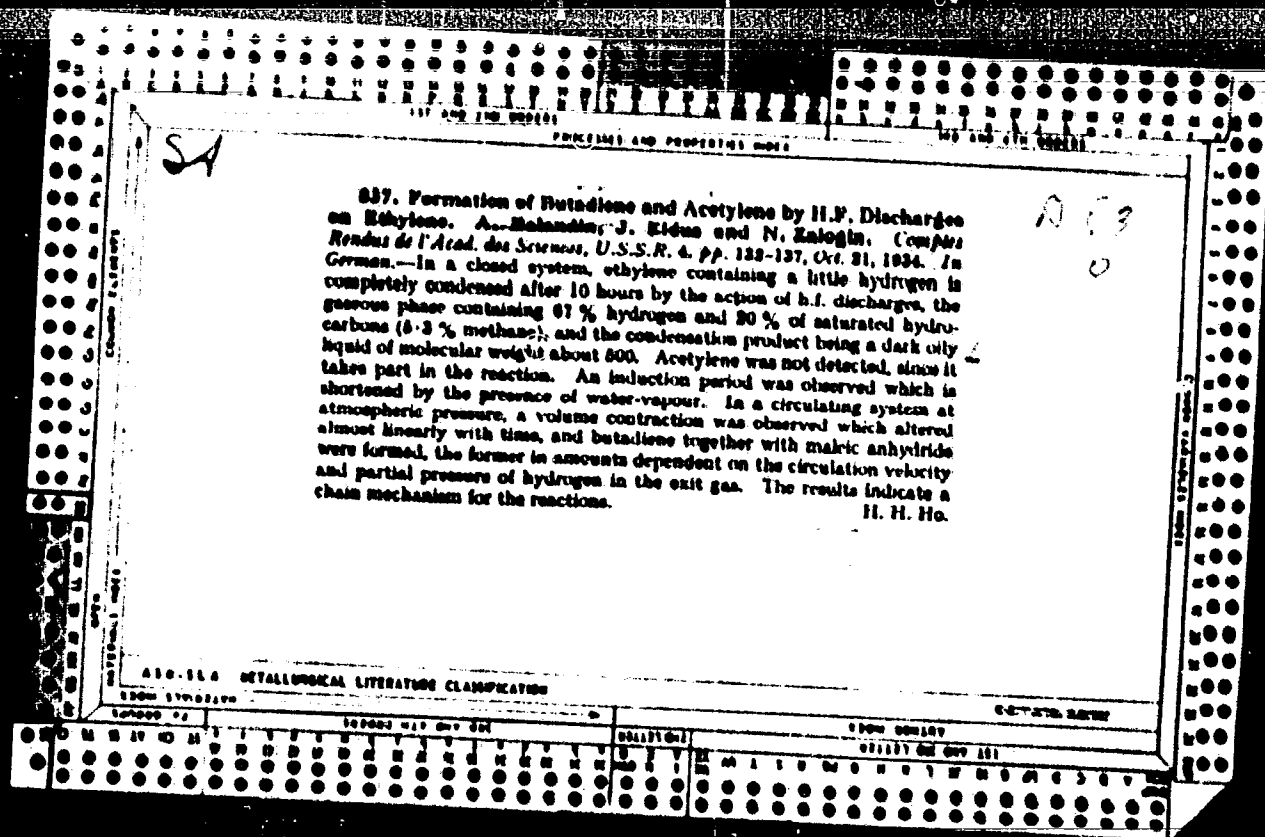
R. Truszkowski.











PROCESSING AND PROPERTIES INDEX

137 AND 138 CONTROLS

2

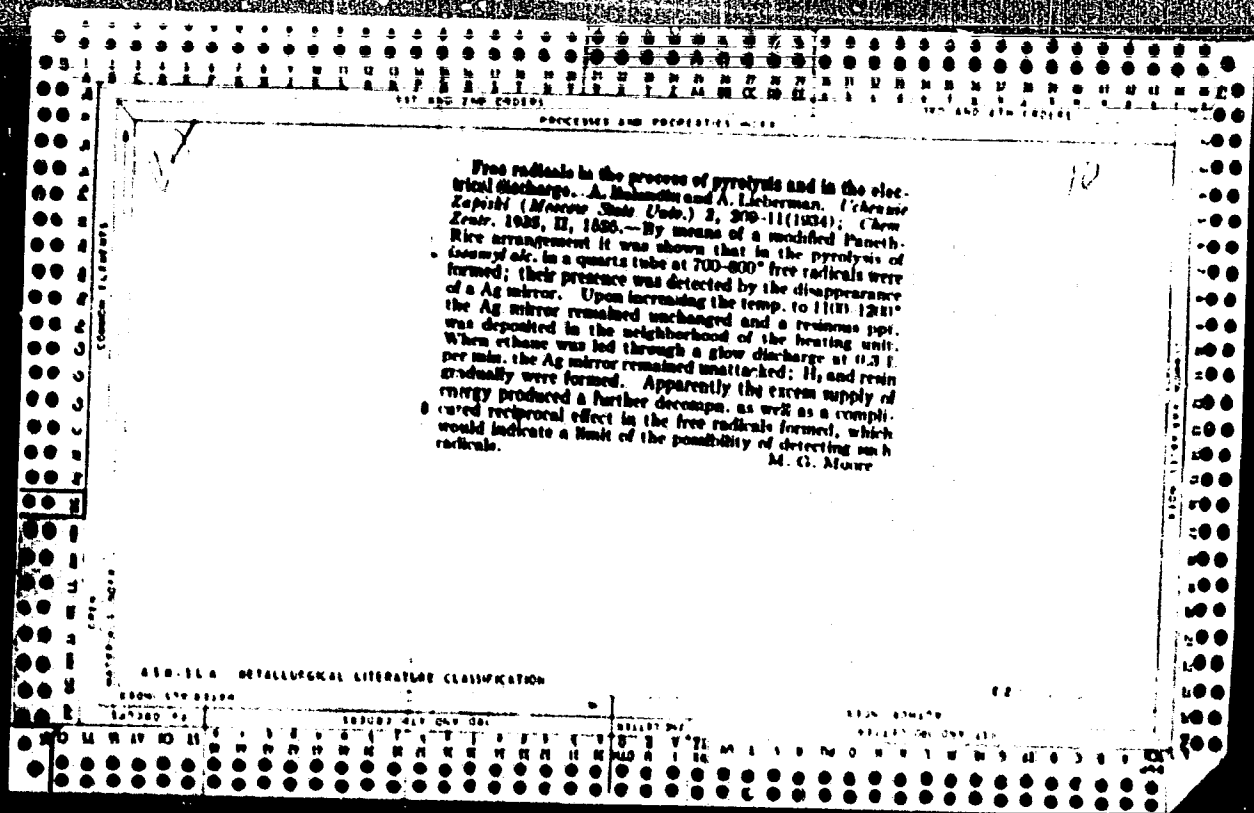
ca

Kinetics of the catalytic dehydrogenation of methylcyclohexane on a nickel-aluminum oxide catalyst. A. A. Zaitsev and N. I. Shukin. *Acta Physicochim. U. R. S. S. R.*, 300-11(1934) (in German). — By the same method as for dimethylcyclohexane (C. A. 28, 7127^o) the energy of activation for mixts. with 0-80% toluene is 12,300 cal. and the value of k_0 in the equation of $k = k_0 e^{-E/RT}$ is 8.8×10^8 in the temp. range 200-350°. Decomposition 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 Komnarski, C. A. 18, 3965) by first dehydrating at 300° and then slowly raising the temp. to 350° 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

ADD SEE METALLURGICAL LITERATURE CLASSIFICATION

137 AND 138 CONTROLS



PROCESSES AND PROPERTIES INDEX

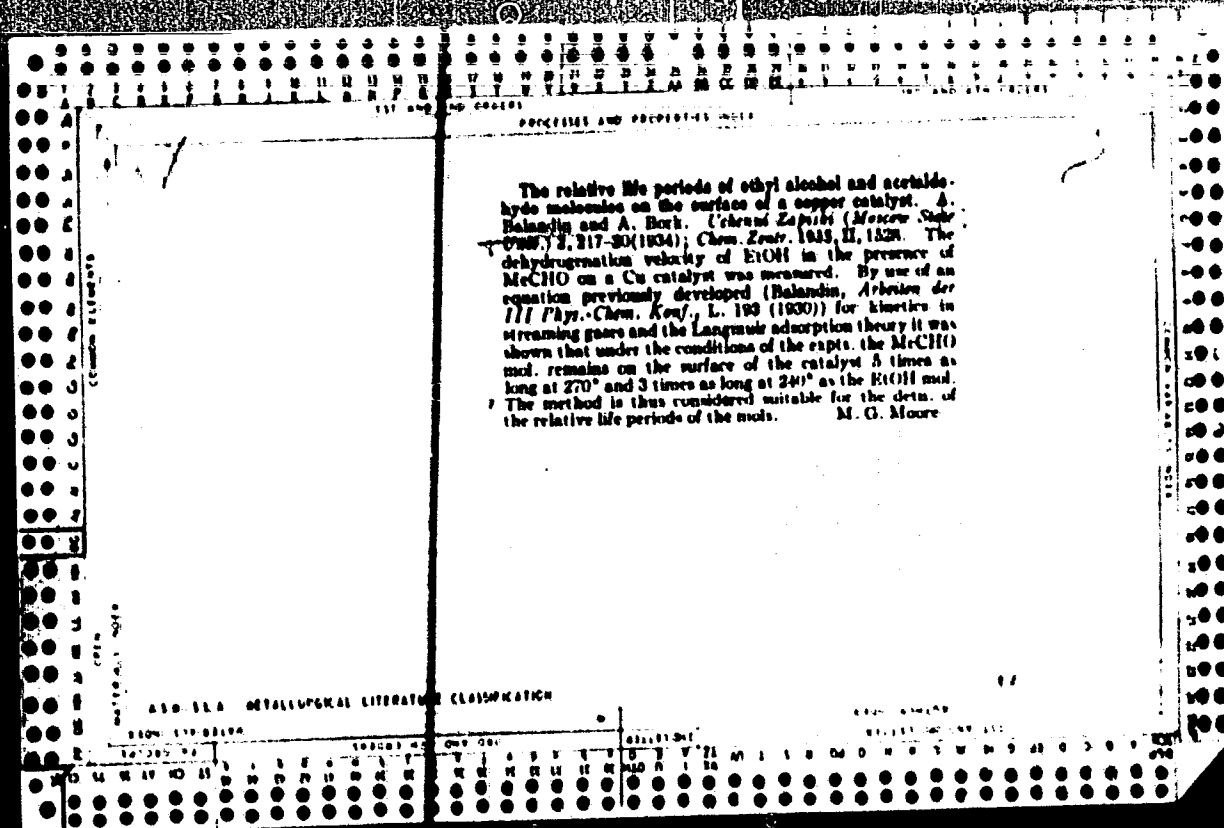
18

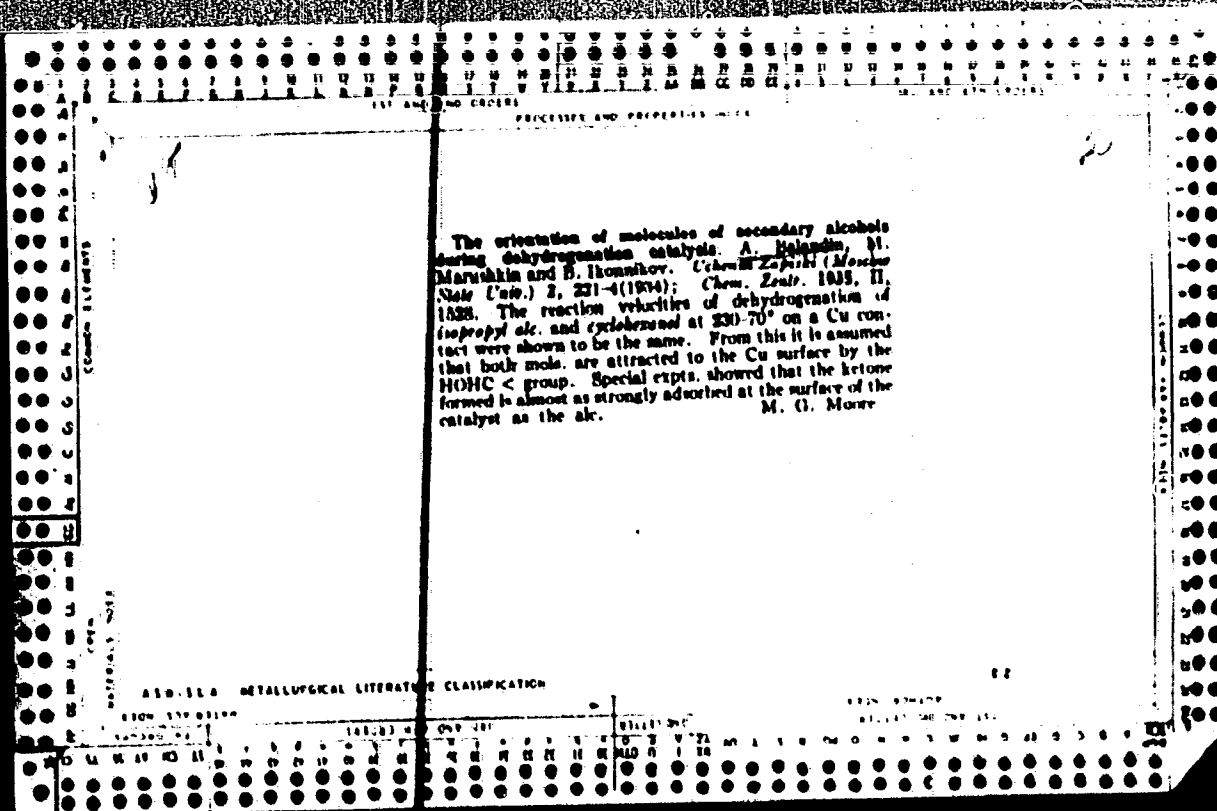
CA

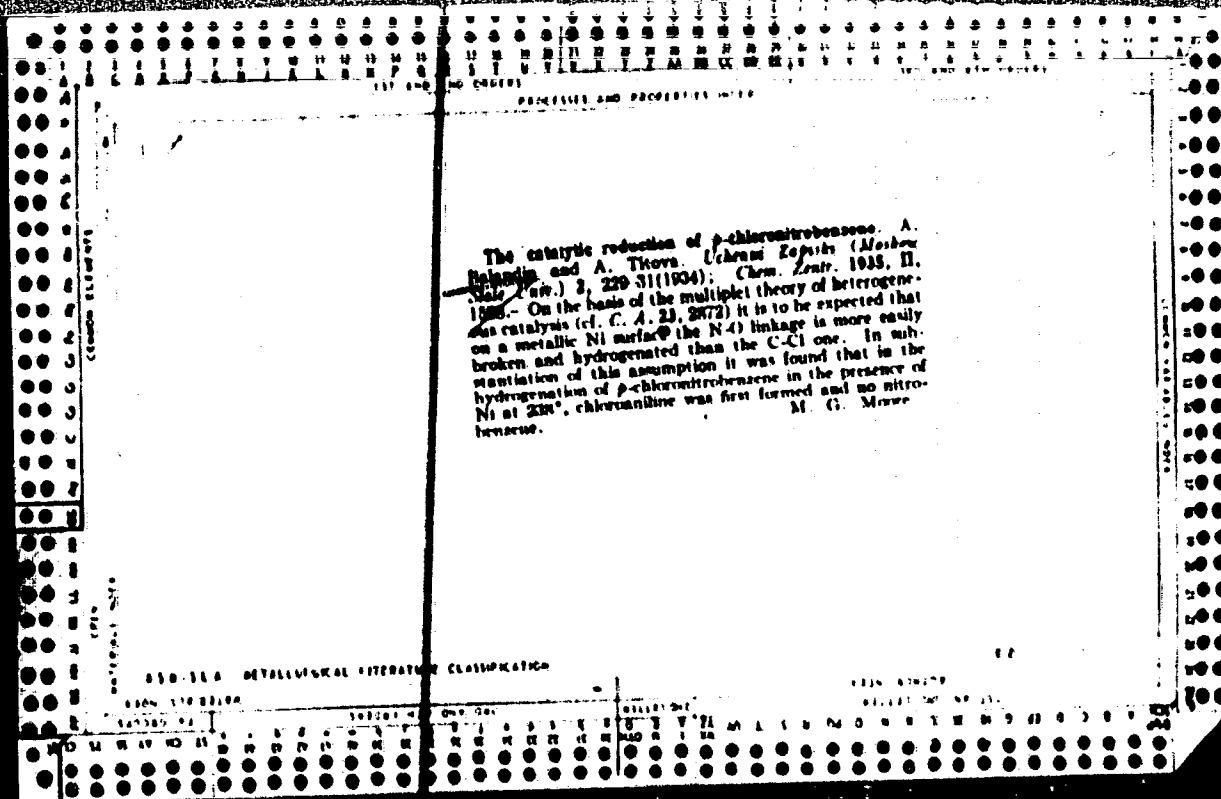
The formation of nitrogen dioxide from nitrogen and oxygen in a high-frequency discharge. A. A. Belandin, Ya. I. Eklus, N. Sibigin and V. Verkhovskii. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1936, 1, 215-16 (1934); *Chem. Zentr.* 1936, 1, 2152. NO_2 is formed in a mixt. of O_2 and N_2 under the influence 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 1 mixt. of N_2 and O_2 is about 5 times as great as from air.

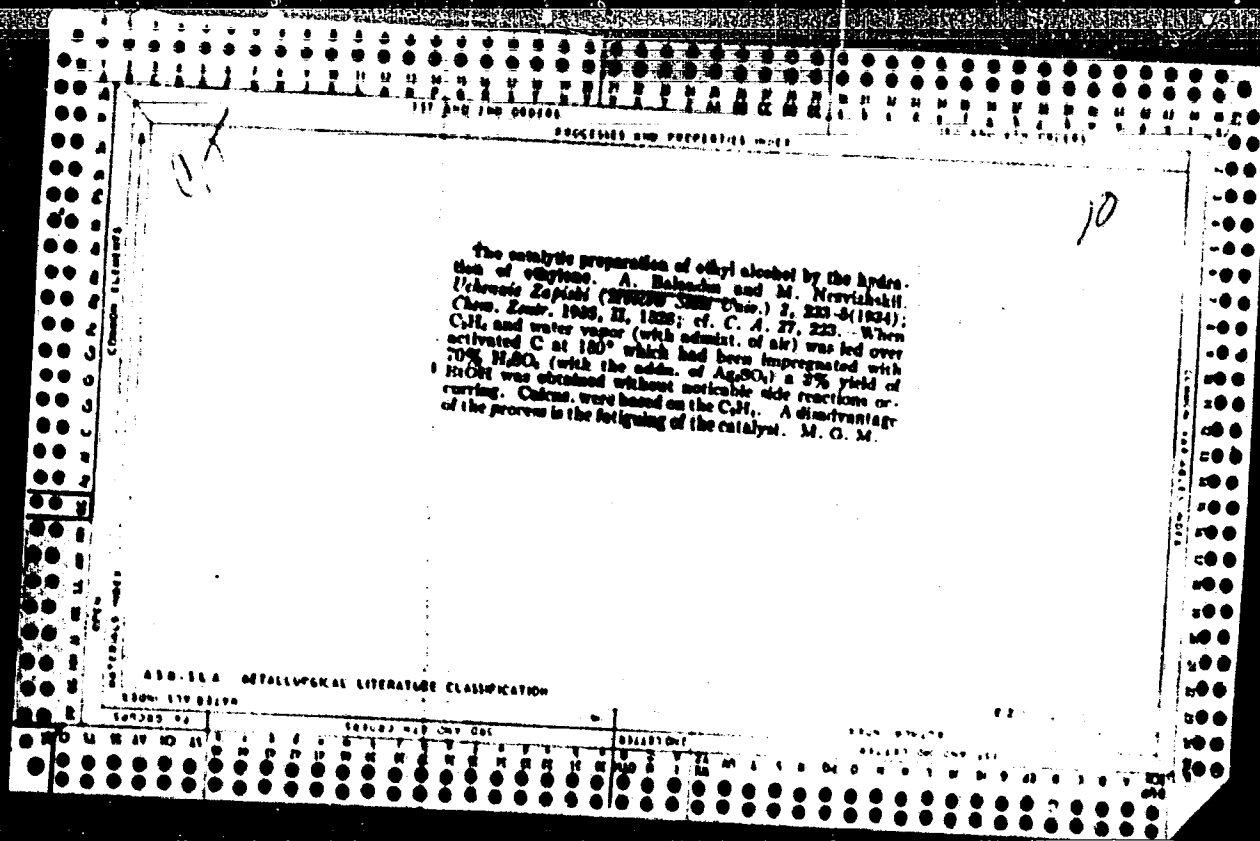
M. G. Moore

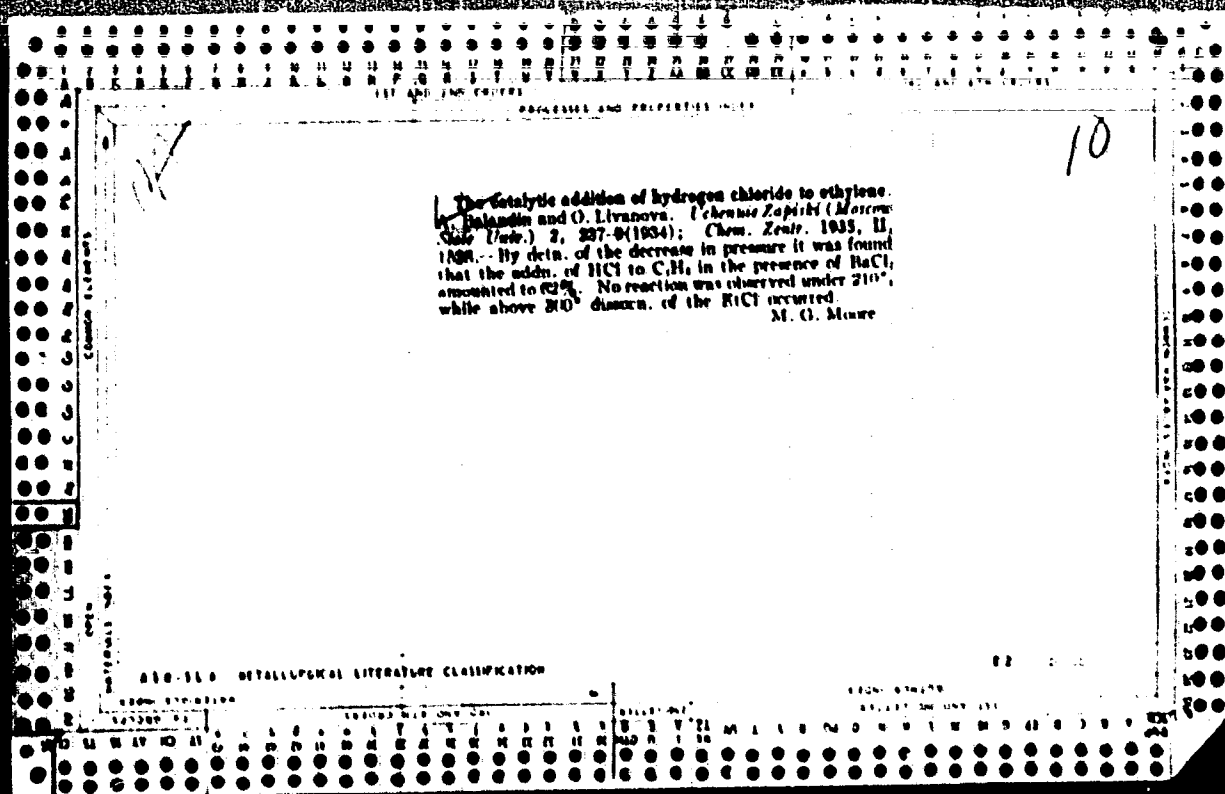
METALLURGICAL LITERATURE CLASSIFICATION











PROCESSING AND REPRODUCTION NOTES

2

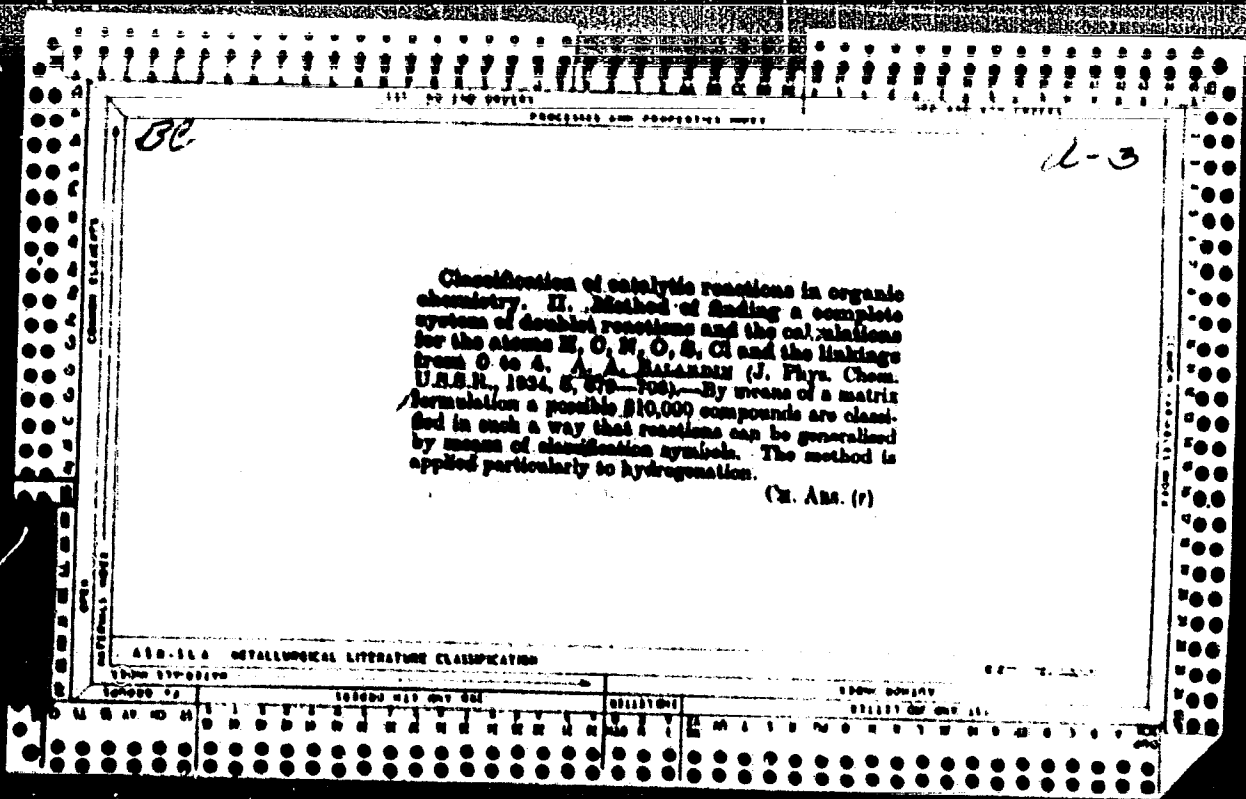
la

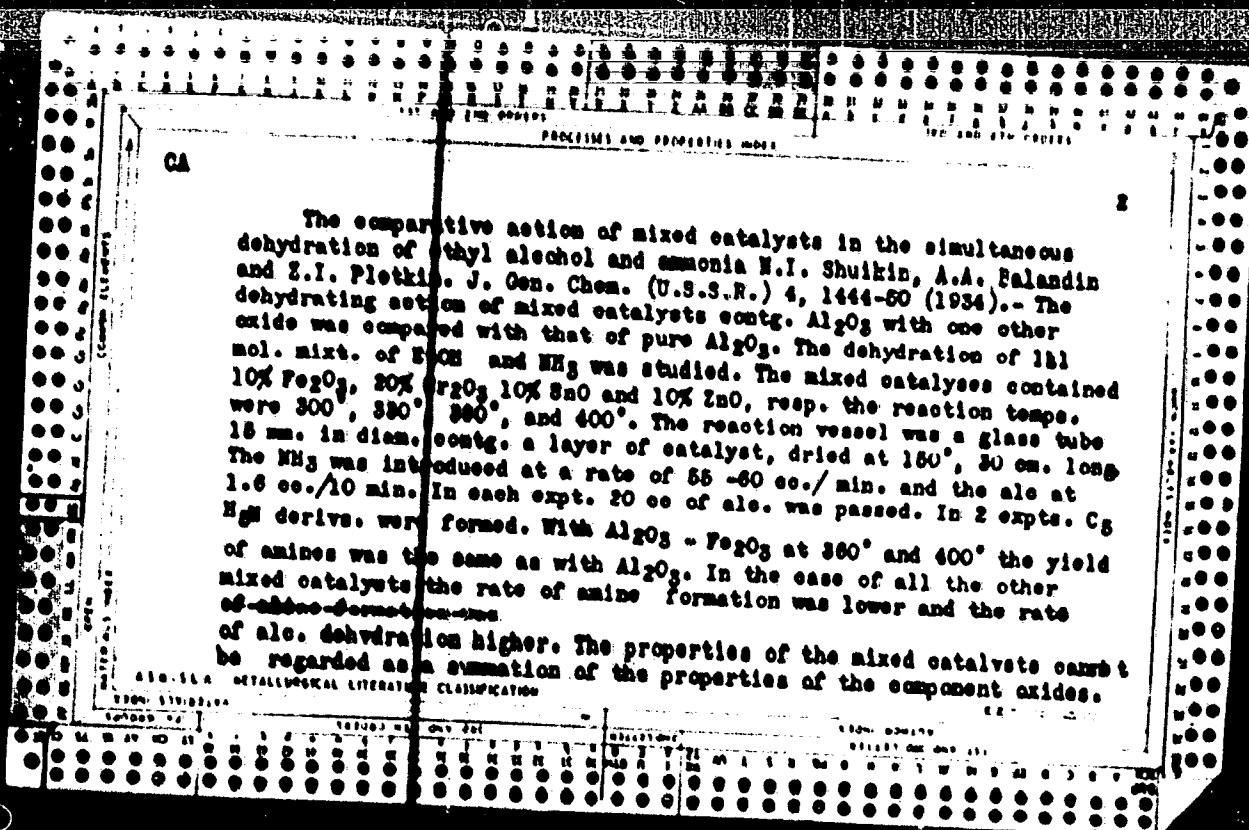
Kinetics of the catalytic dehydrogenation of dimethylcyclohexane. A. A. Dolandis and Yu. K. Yur'ev. *J. Phys. Chem. (U. S. S. R.)* 8, 303-400(1934).—The speed of the reaction on Ni and Al oxide catalysts was studied as a function of temp. and of the initial concns. of the di-

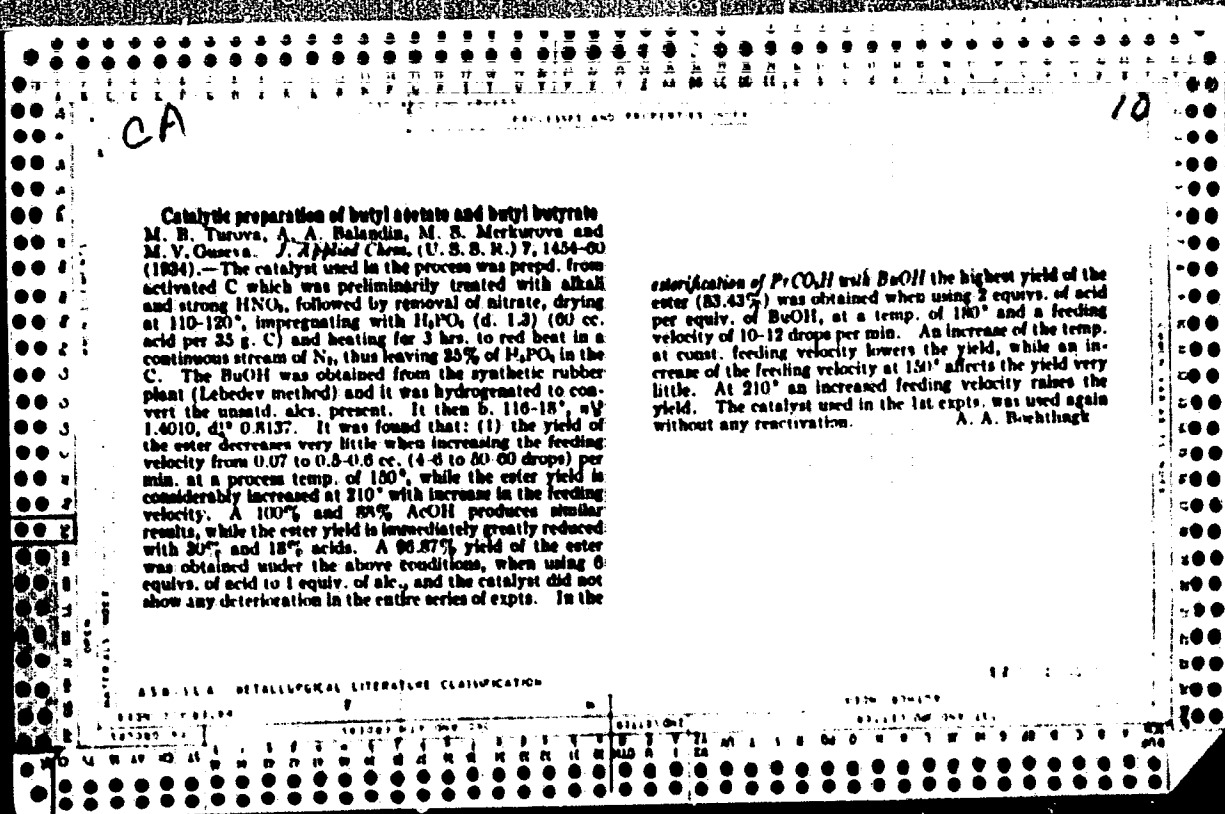
dimethylcyclohexane (I)—ylene (II) mixts. (consisting of both cases of all three isomers). For all mixts. contg. 0-100% I the energy of activation from 2411 to 3301 kcal. per mol. but falls to 12,300 in a 10% mixt. Methane formation is slight if I is pure. The rate of dehydrogenation of I is slightly greater than that of cyclohexane. The analyses were made by means of refractive indexes, which are practically a linear function of the compo. of the mixt. of I and II. F. H. Rathmann

METALLURGICAL LITERATURE CLASSIFICATION

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	00
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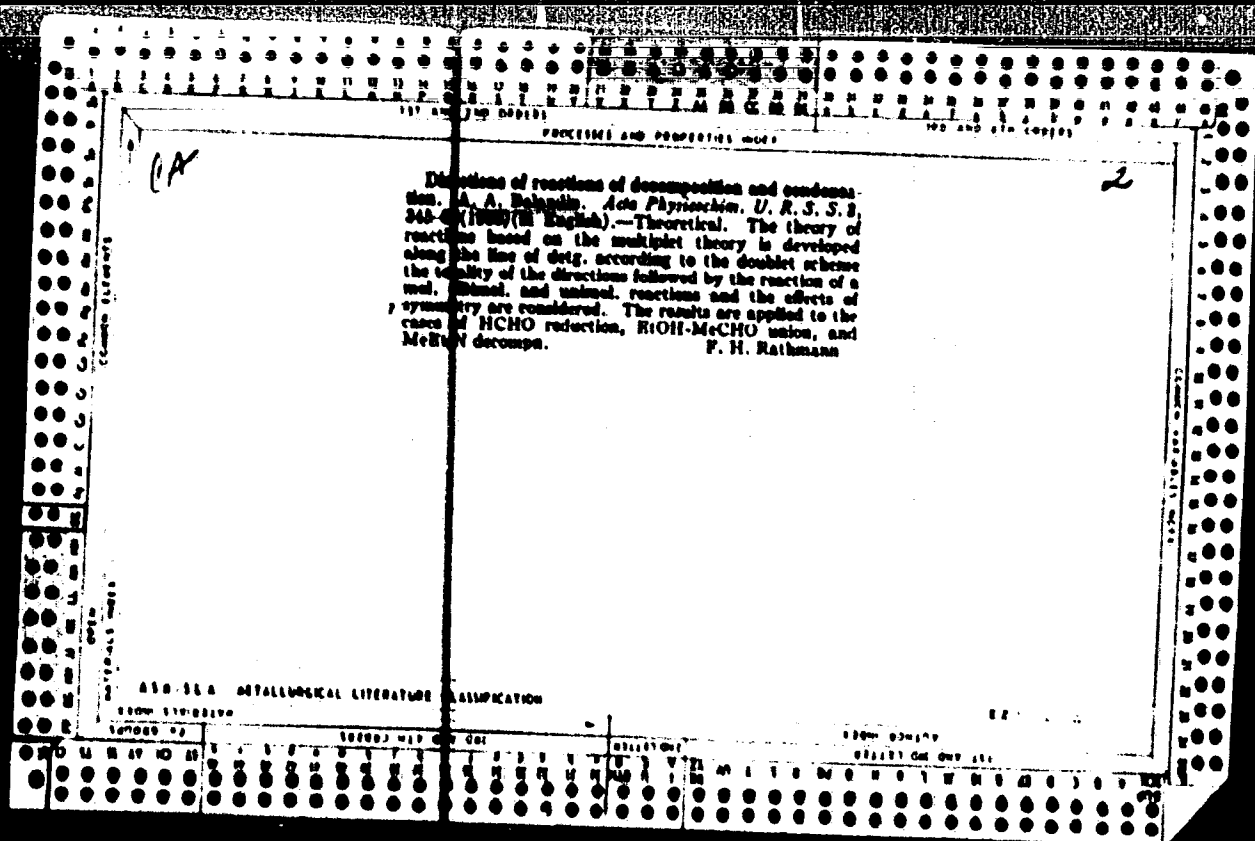
BC a-1

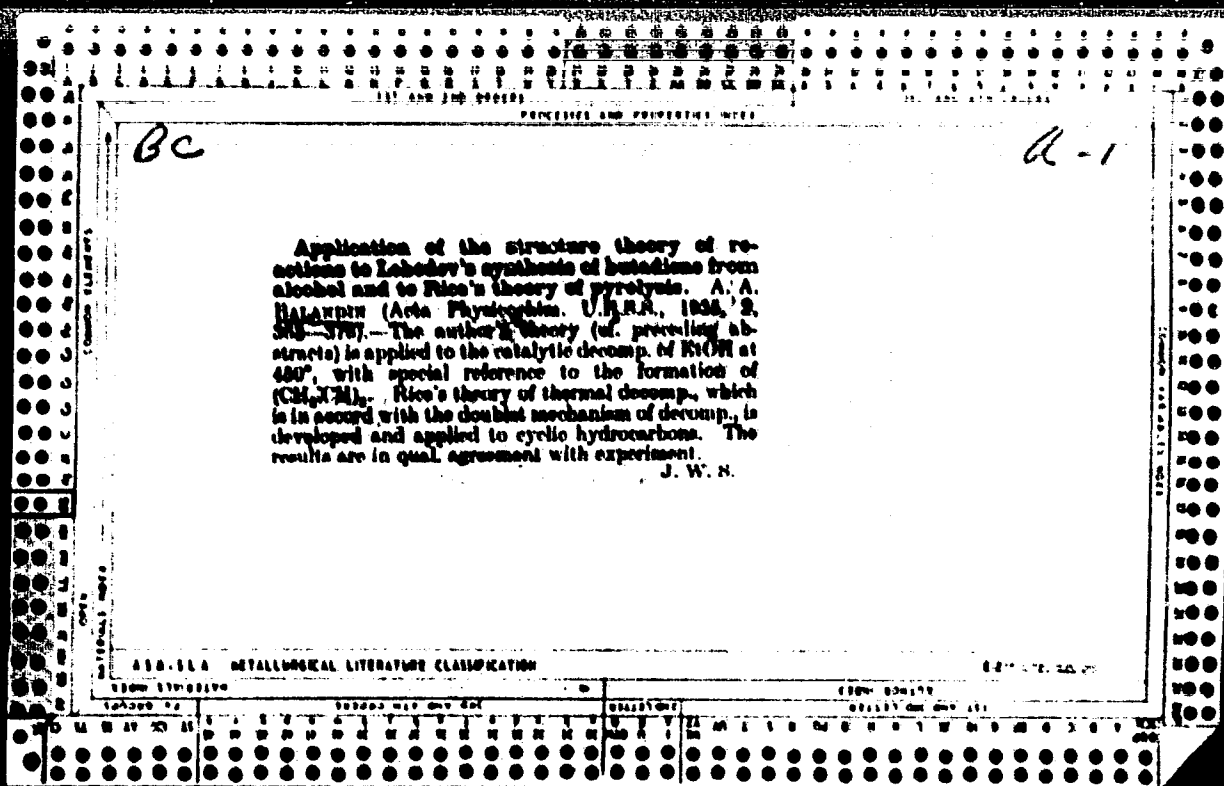
PROCESSED AND REPRODUCED BY THE NATIONAL ARCHIVES

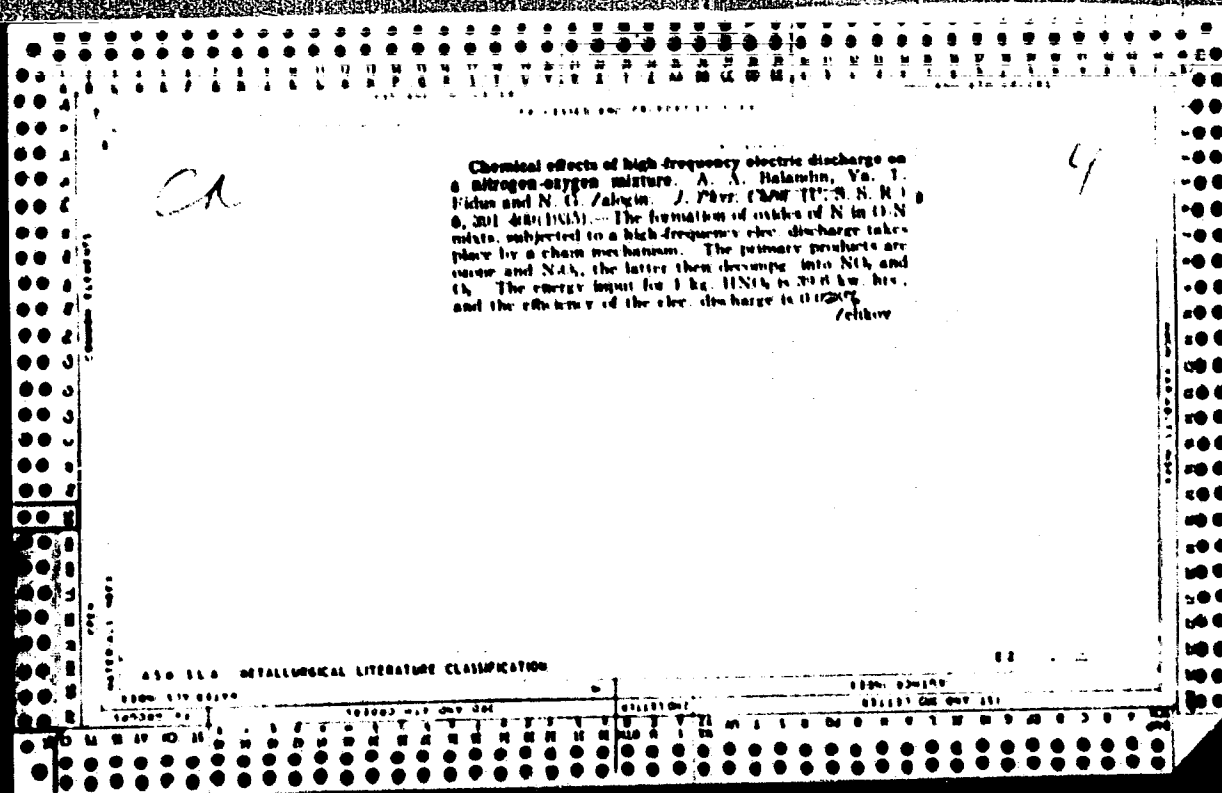
Structure theory of chemical change. Complete system of doublet reactions. A. A. BALAN-DIX (Acta Physicochim. U.R.S.S., 1935, 2, 177-202; cf. "A." 1935, 519, 890).—A complete system of "doublet" reactions in org. chemistry is drawn up. All have not been experimentally realized. The theory of structure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

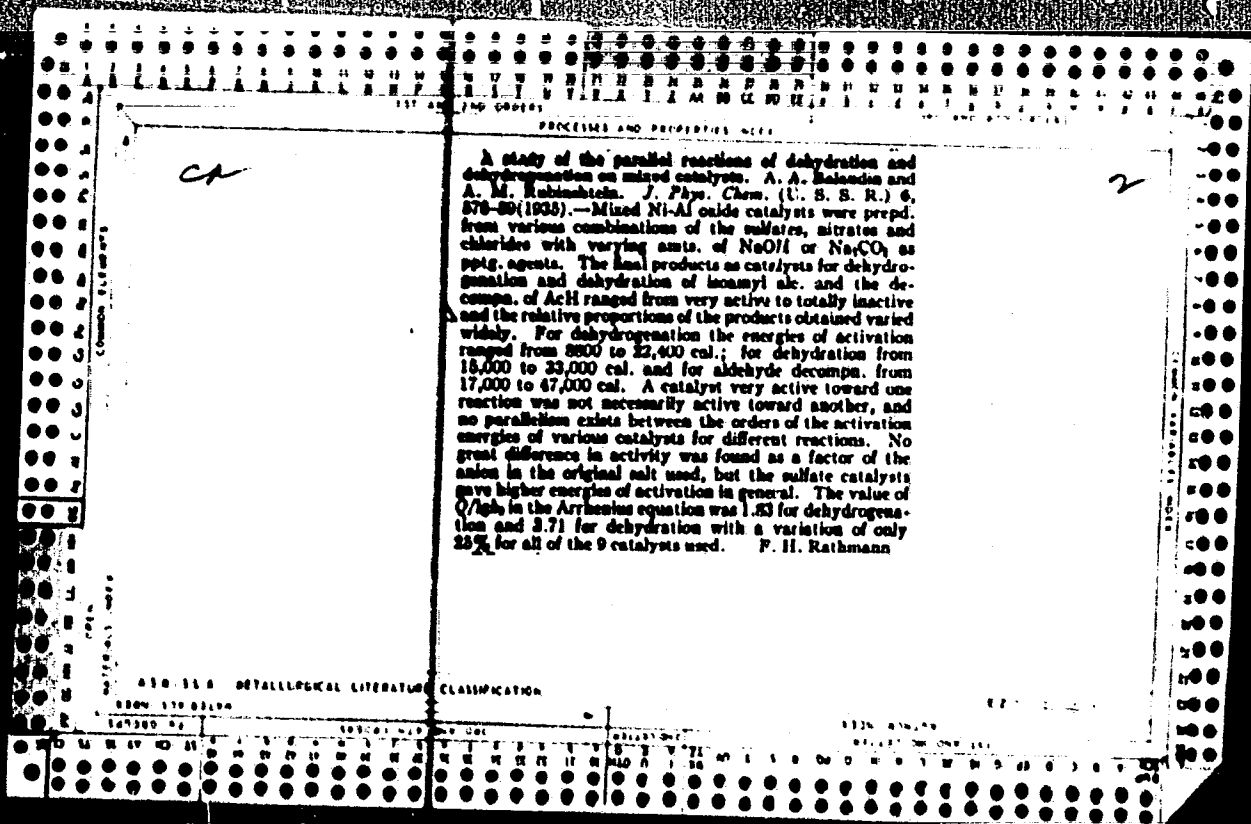
ASS. S.L.A. METALLURGICAL LITERATURE CLASSIFICATION

10000 00-100	10000 00-100	10000 00-100	10000 00-100
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PROCESSES AND PROPERTIES INDEX

B. A. P. H. K. 2

Present position of the problems of catalysis and the theory of multiplets. A. A. Tolandin, *Uspehi Khim.* 6, 1004-57(1925).--The development of the multiplet theory of catalysis on the basis of data obtained by B. and by others (cf. C. A. 23, 277, 8000; 24, 4084, 6085) is discussed, and new unpublished data are added. The multiplet theory is applied to both the phys. and the chem. aspects of catalysis. Quantum-mechanically its foundations were strengthened by Polanyi (cf. C. A. 23, 4265). The shapes of molecules during dehydrogenation and hydrogenation catalysis and of the corresponding crystal lattices of the catalysts are considered on the basis of new work. Energetic factors are taken into account. The theory predicts the course of catalysis for various chemical reactions. A complete system of doublet reactions is given, and serves for classification purposes. As an example, by its help the as yet unknown reactions of the hydrogenation hydrolysis of acid *N*-sulfonamides are predicted. The results are generalized to a structural theory of reactions and a consideration of the structure theory of compounds. Index groups of atoms in contact with the catalyst are distinguished. Specific catalysis depends on their orientation to the catalyst. The problems of studying the relation of these indexes to the analogous functional groups of the classical structure theory is presented. Kaptl. examples of such studies on the hydration, amination and alkylation (cf. C. A. 27, 225, 20, 645) are brought forward. The math. theory of the direction of decomposition of condensation of molecules is considered (cf. *Acta Phys. (Chem.)* 3, 177(1935); C. A. 20, 6494). By this means the multiplet theory is applied to the synthesis of divinyl from alca. where up to C, about 2) different products are formed. The most recent data (C. A. 20, 4320) 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, 1202; 28, 2255; 20, 2505; *Acta Physicochim. U. R. S. S. R.* 1, 184(1934); C. A. 20, 6120).
A. A. Tolandin and
F. H. Mathmann

METALLURGICAL LITERATURE CLASSIFICATION

1930-1939

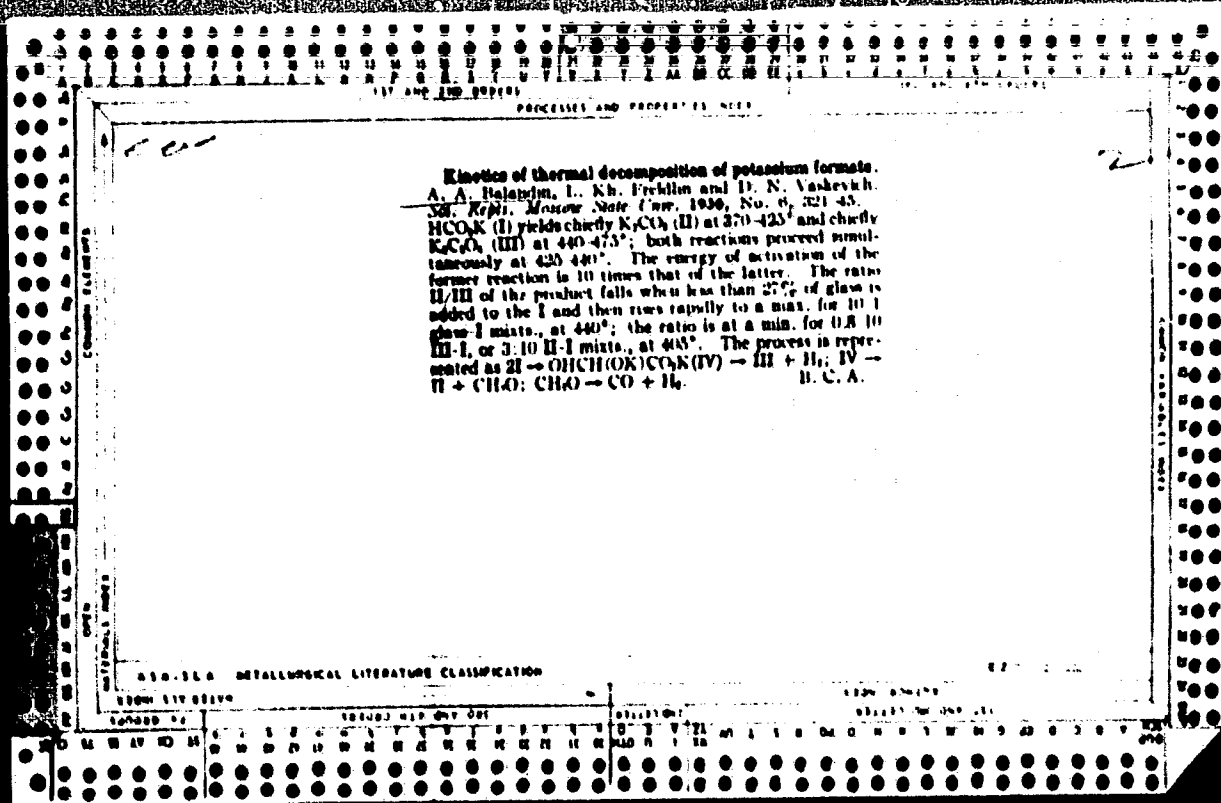
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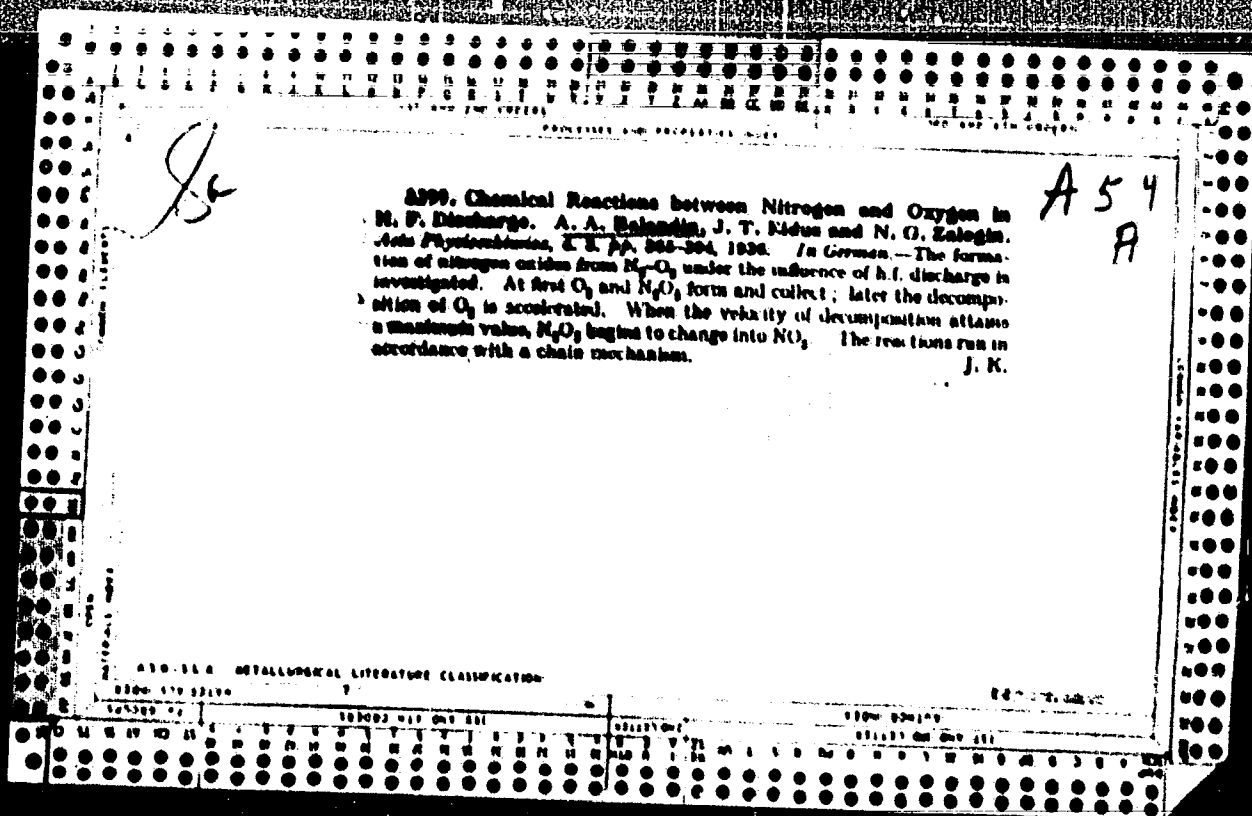
8-3

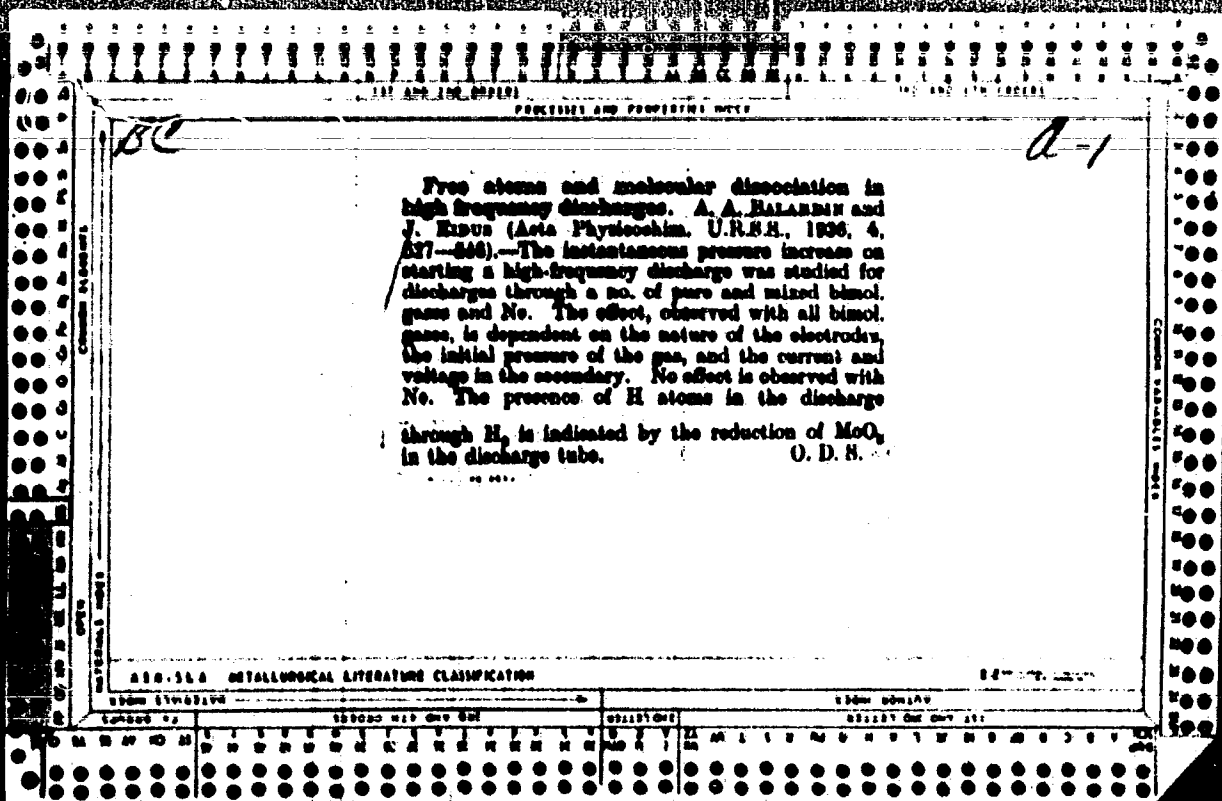
Influence of substituents on the velocity of catalytic dehydrogenation of cyclohexane derivatives. II. A. A. BALABAN and N. I. SOKOLIN (Sci. Rep. Moscow State Univ., 1968, No. 6, 281-288).—The velocity of dehydrogenation of methylcyclohexane at 200–250° (Ni-Al₂O₃ catalyst) is slightly > that of cyclohexane. R. T.

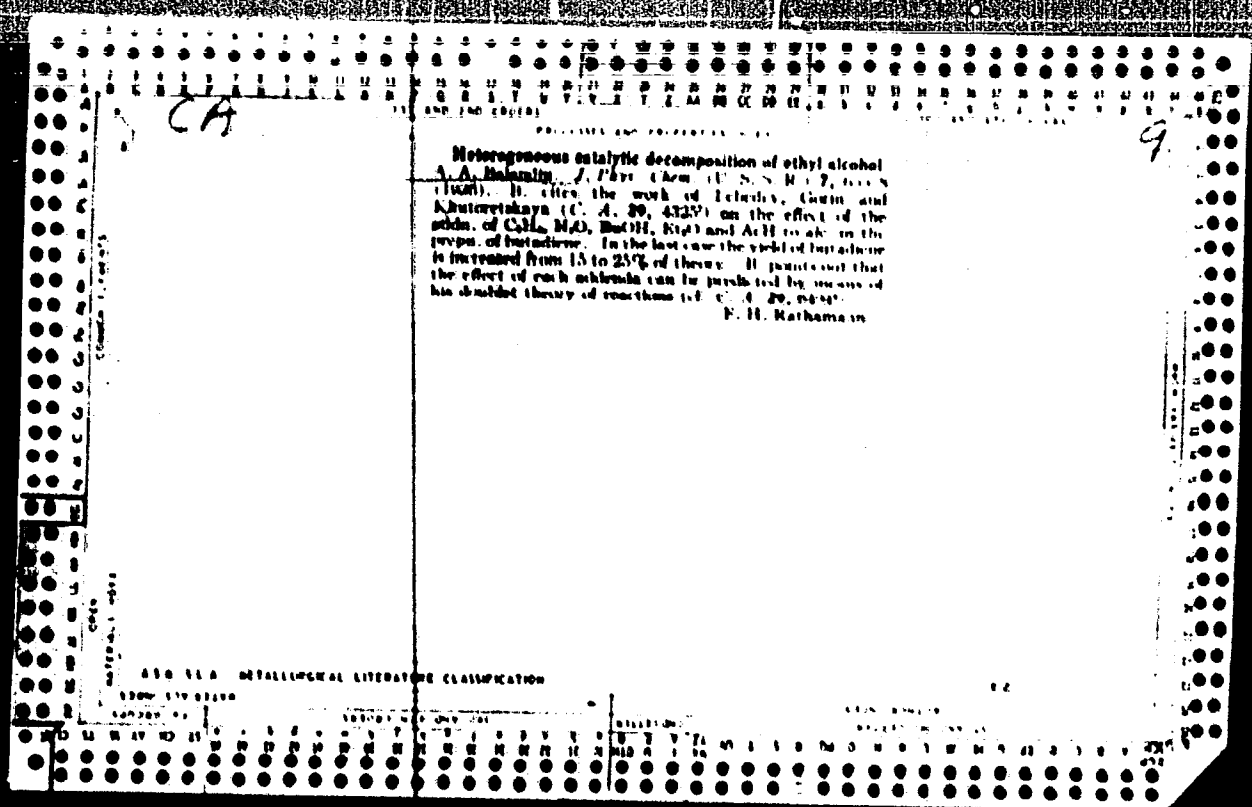
450-51.6 METALLOGICAL LITERATURE CLASSIFICATION

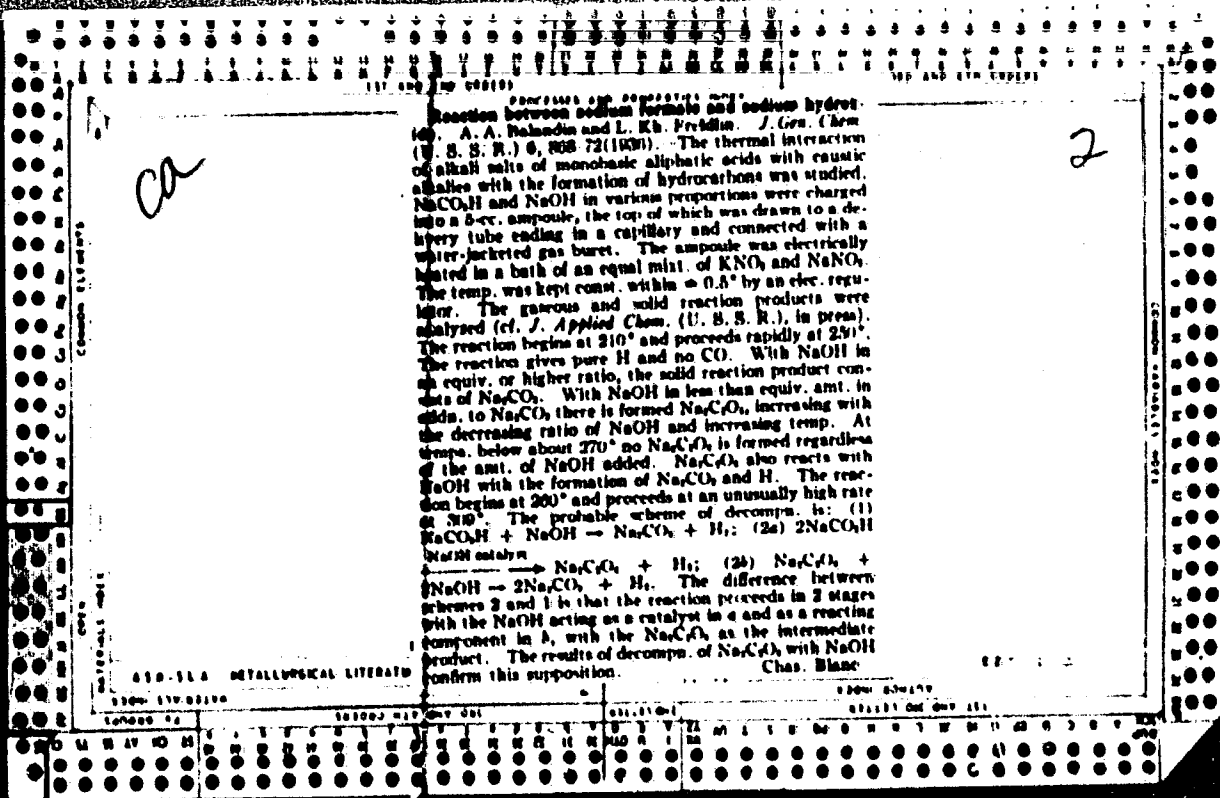
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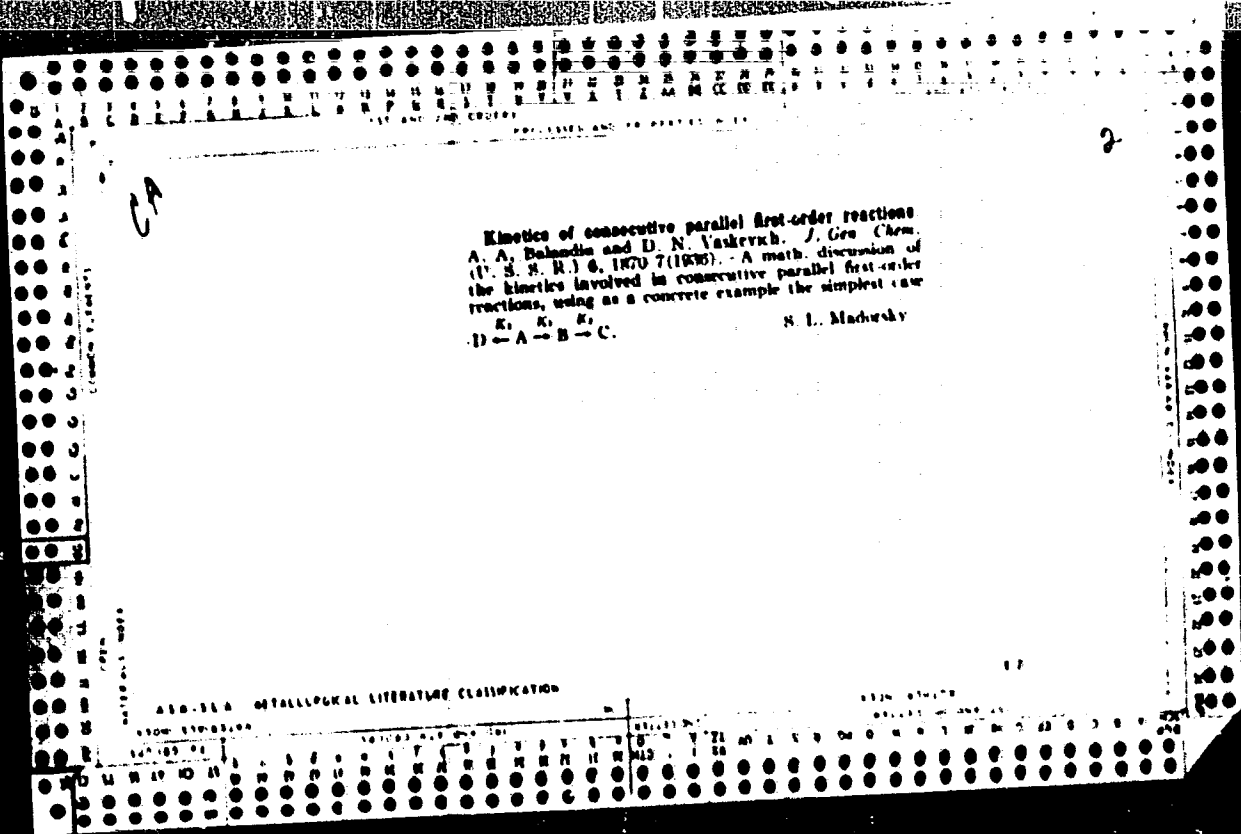


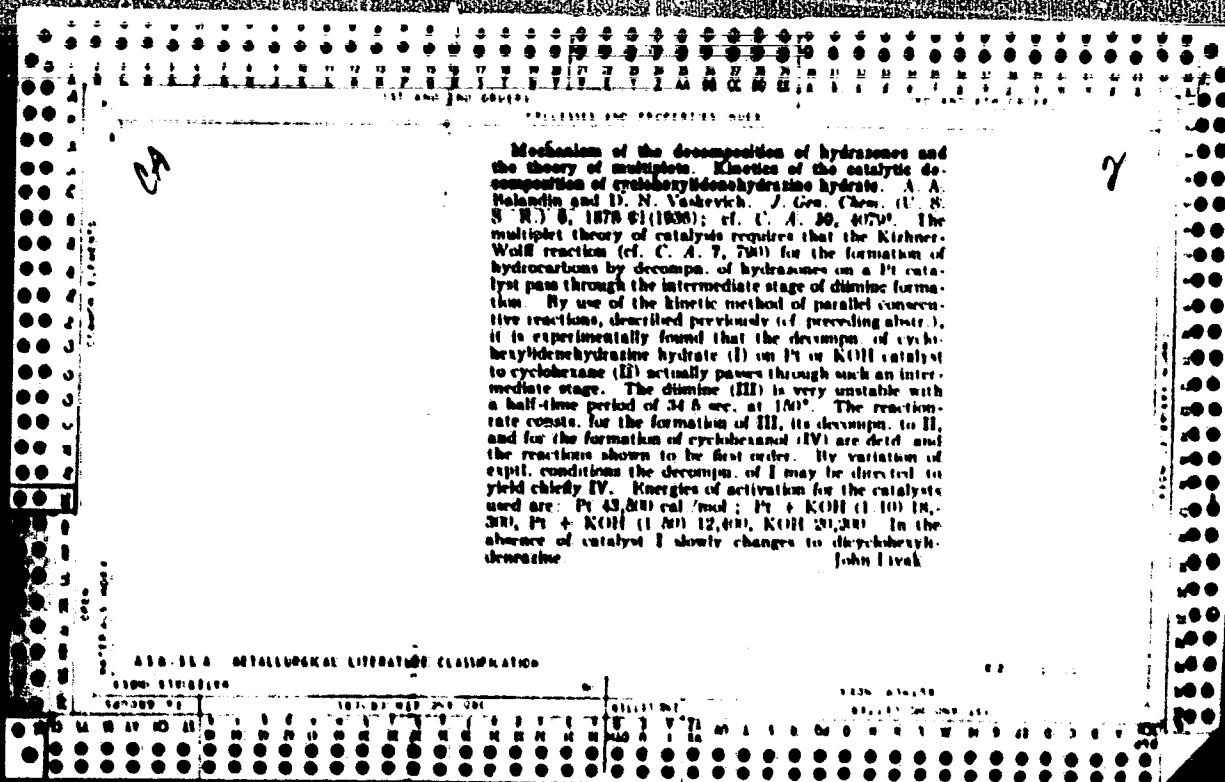






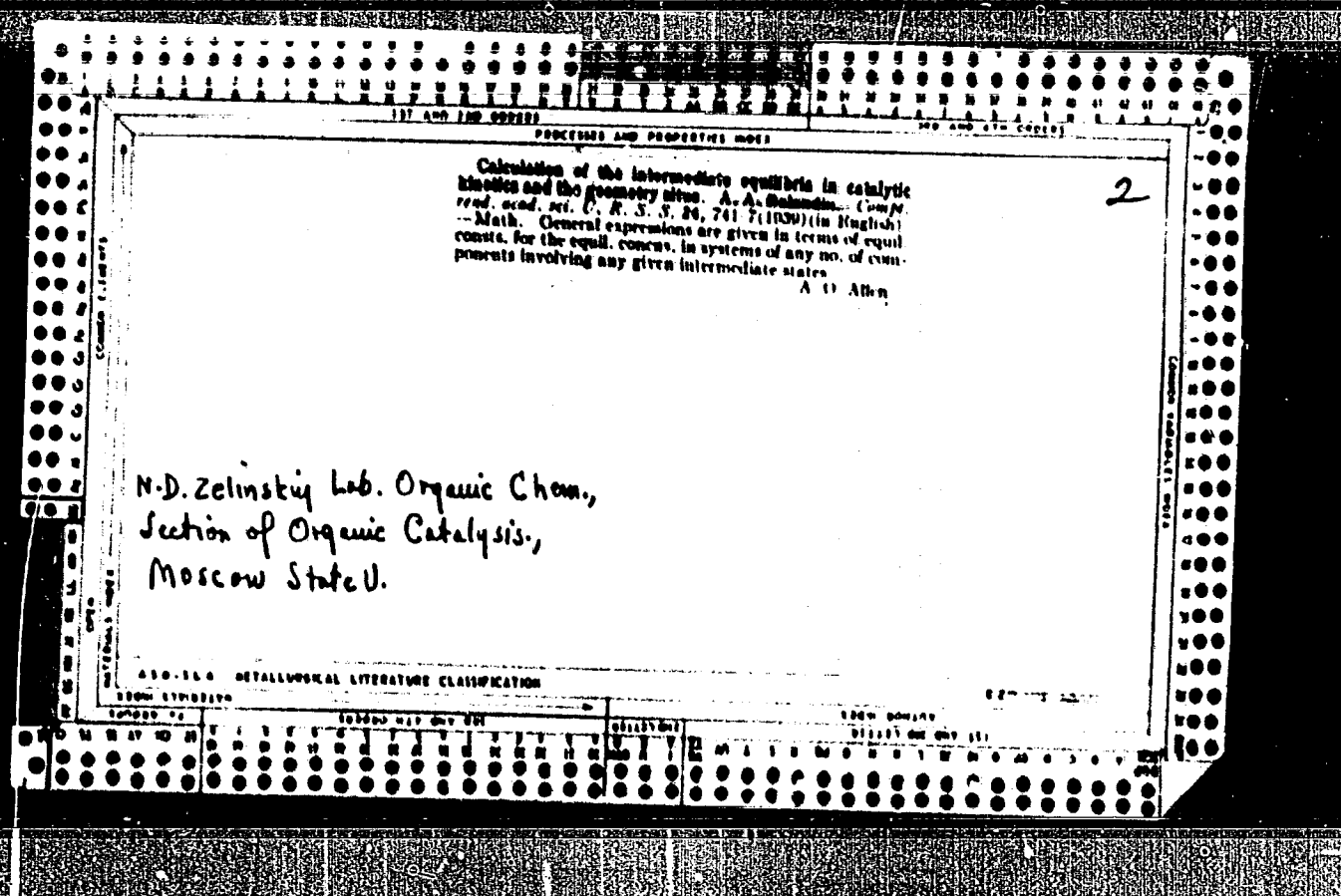


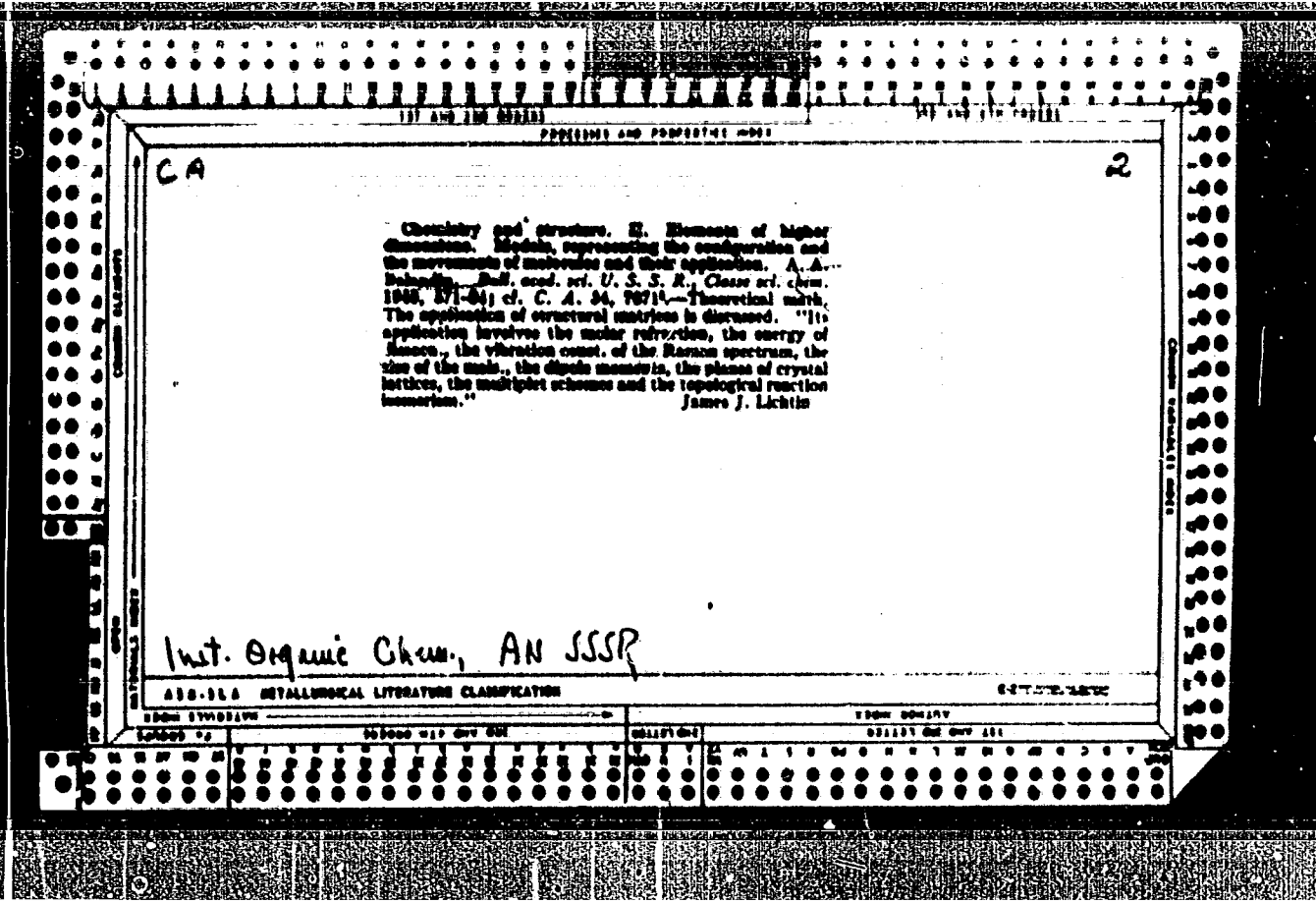




"Catalyse de deshydrogenation du cyclohexane en presence de l'oxyde de chrome." Balandine,
A. A. (p. 18)

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





PROCEDURES AND PROPERTIES INDEX

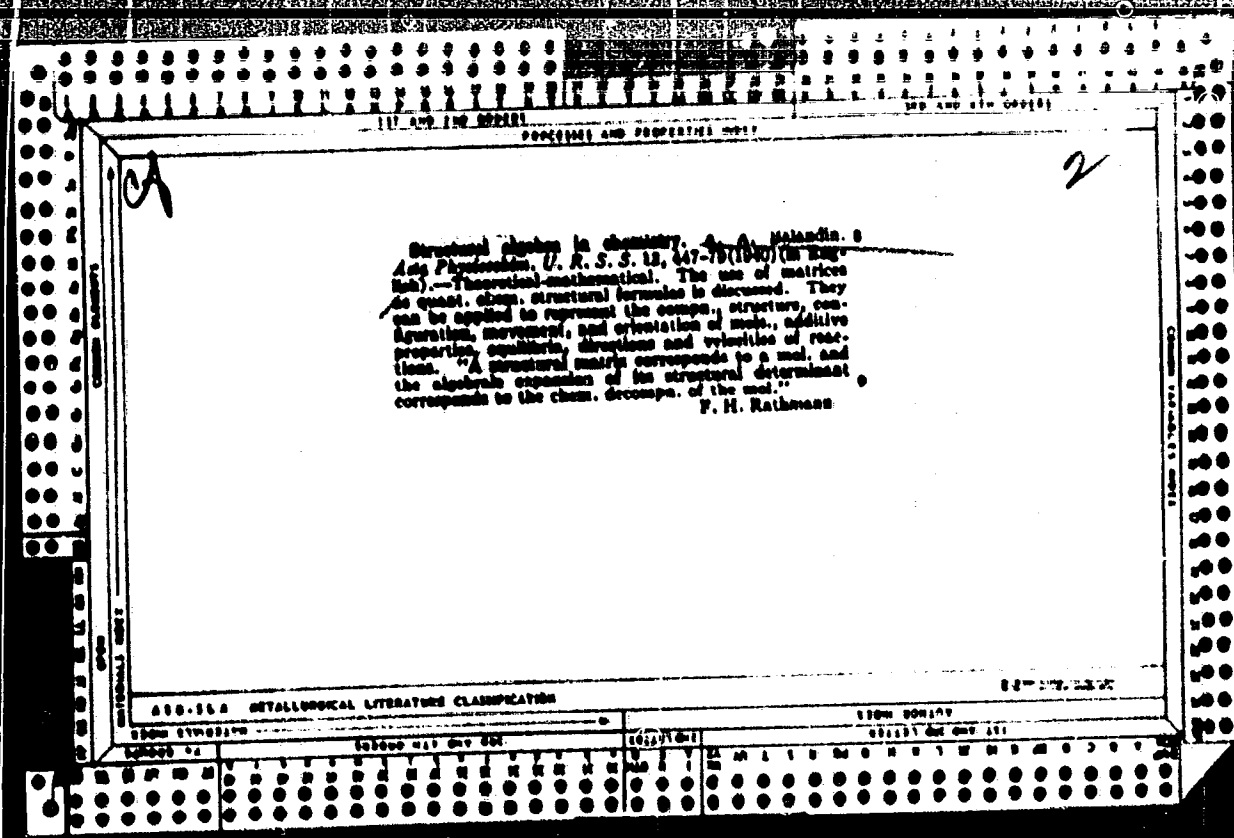
BC A-1

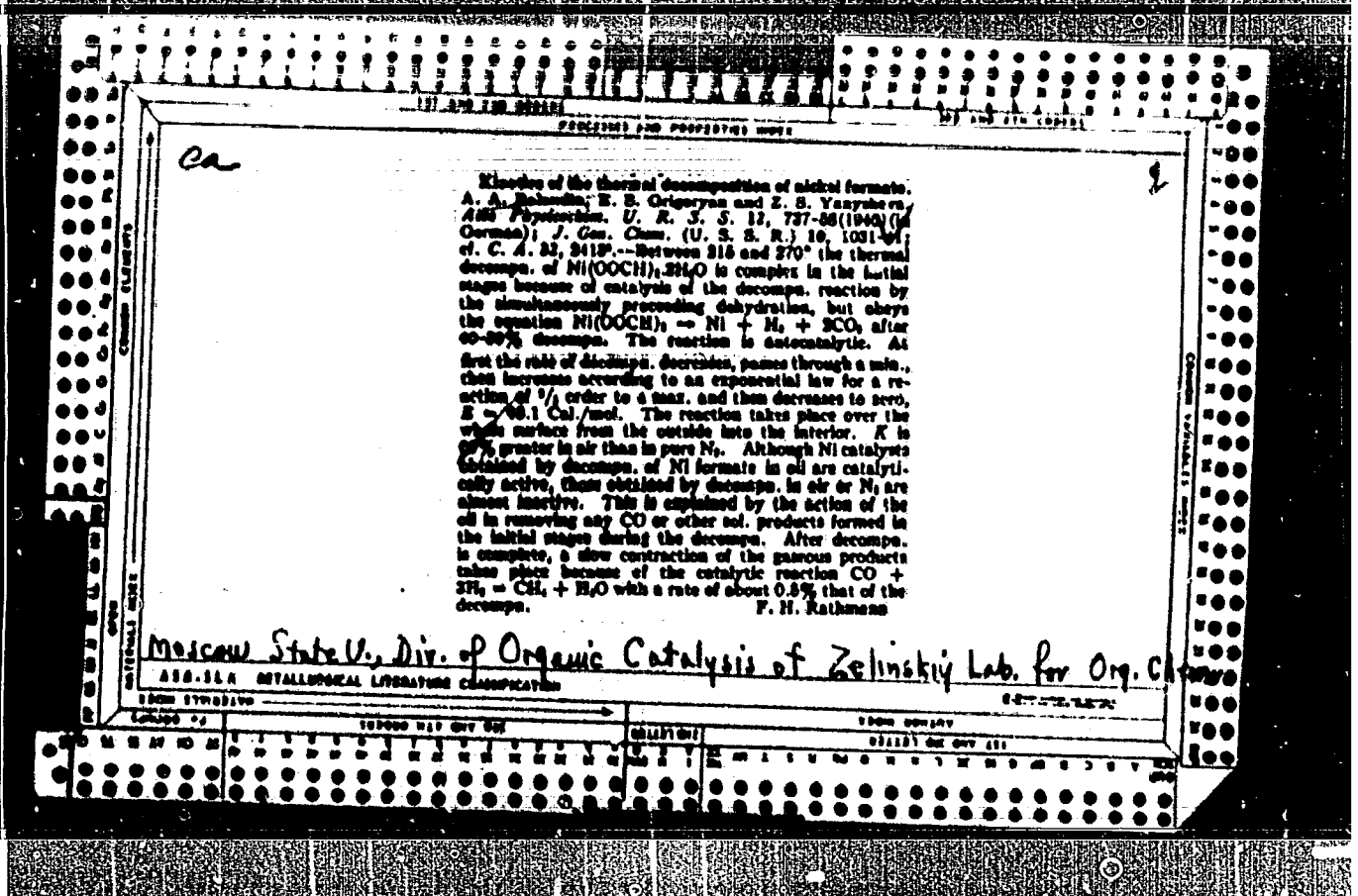
Thermal transformations of Oxalates. L. C. Froid-
 Ma, A. A. Polozin, and A. I. Lobedevs (*Bull. Acad. Sci. U.R.S.S. Chem. Ser. Chem.* 1960, 988-993).—The reactions
 (I) $2\text{HCO}_2\text{Ti} \rightarrow \text{Ti}_2\text{CO}_3 + \text{CO} + \text{H}_2$, (II) $2\text{HCO}_2\text{Ti} + \text{CO}_2 + \text{H}_2 \rightarrow \text{Ti}_2\text{CO}_3 + \text{CO} + \text{HCO}_2\text{H}$ take place at
 210–270°; reactions (III) and (IV) are favoured by rising
 temp. and by dehydrogenation catalysts (Pt-black, Os-
 carbonyl). Oxalate is not produced under any conditions.
 (I) reacts with NaNH_2 at 97° or CaO at 130–220° as follows:
 $2\text{HCO}_2\text{Ti} + 2\text{NaNH}_2 \rightarrow \text{Na}_2\text{C}_2\text{O}_4 + \text{NaOH} + \text{Ti}_2\text{CO}_3 + \text{H}_2$;
 $2\text{HCO}_2\text{Ti} + \text{CaO} \rightarrow \text{CaC}_2\text{O}_4 + \text{Ti}_2\text{CO}_3 + \text{H}_2$; whilst with Ac_2O at 80°
 the reaction is $\text{Ac}_2\text{O} + \text{HCO}_2\text{Ti} \rightarrow \text{TiAc} + \text{AcOH} + \text{CO}$.

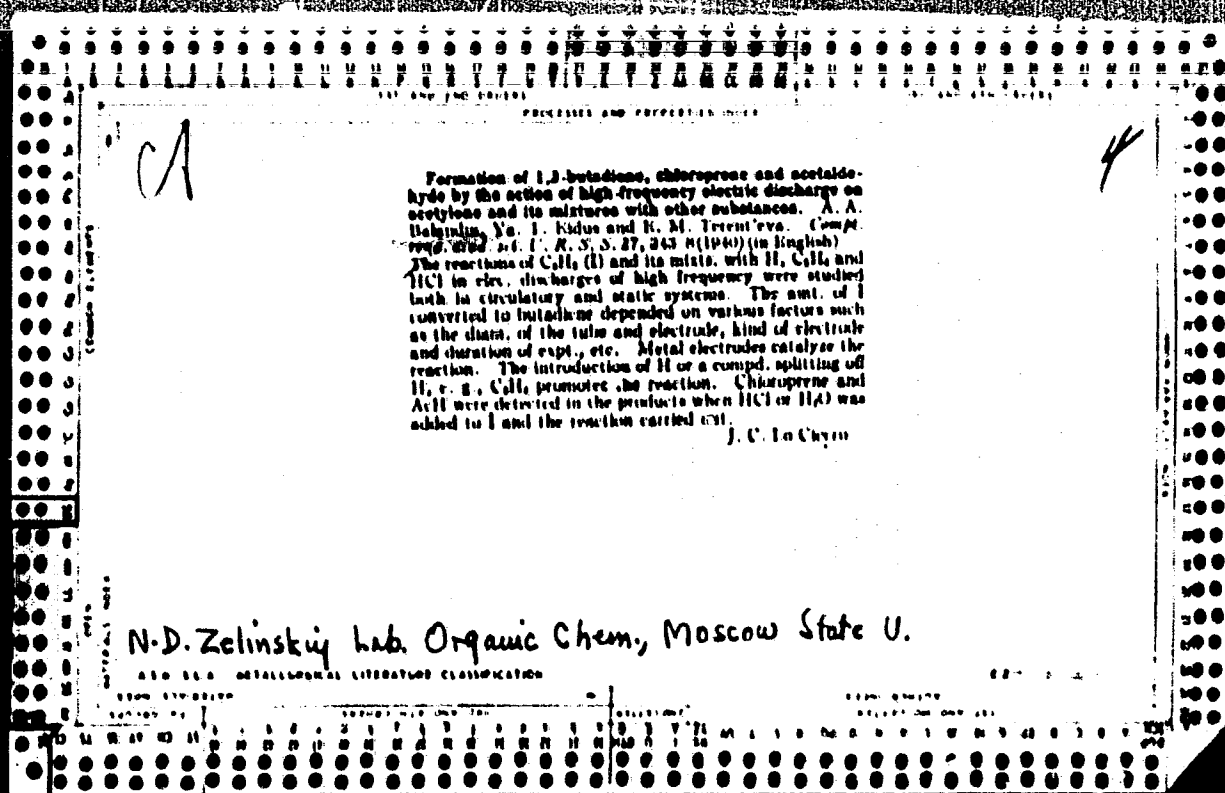
R. T.

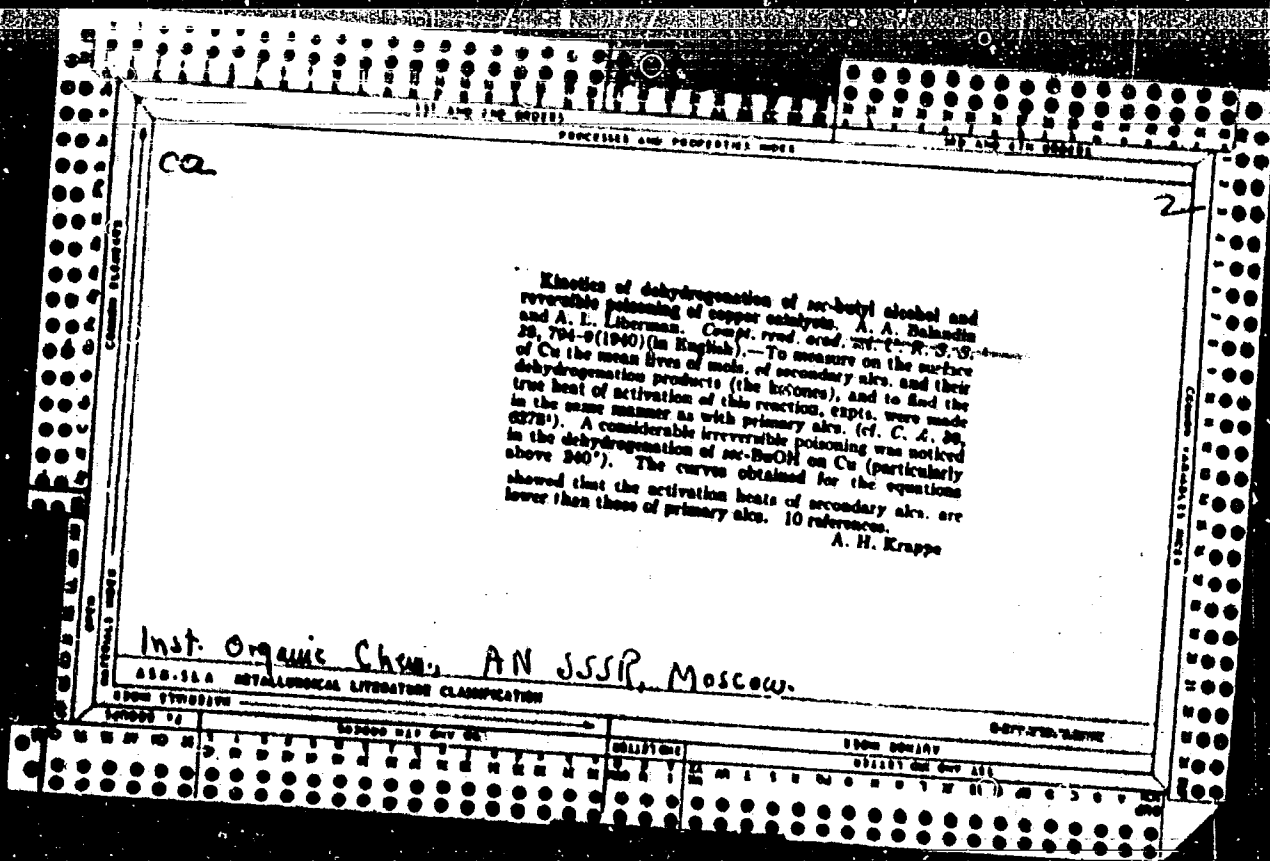
Inst. Organic Chem., AN SSSR

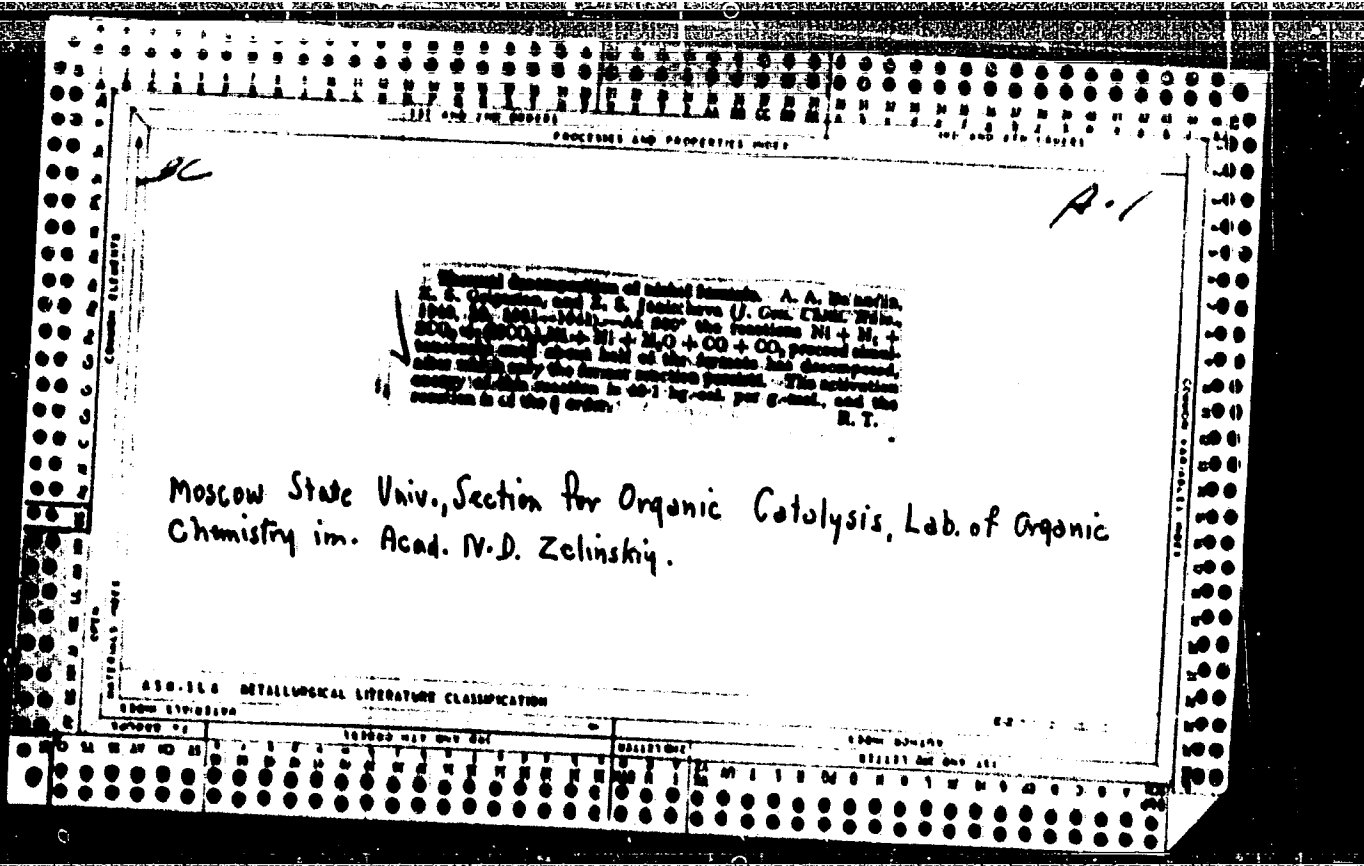
ASD. 51A METALLURGICAL LITERATURE CLASSIFICATION

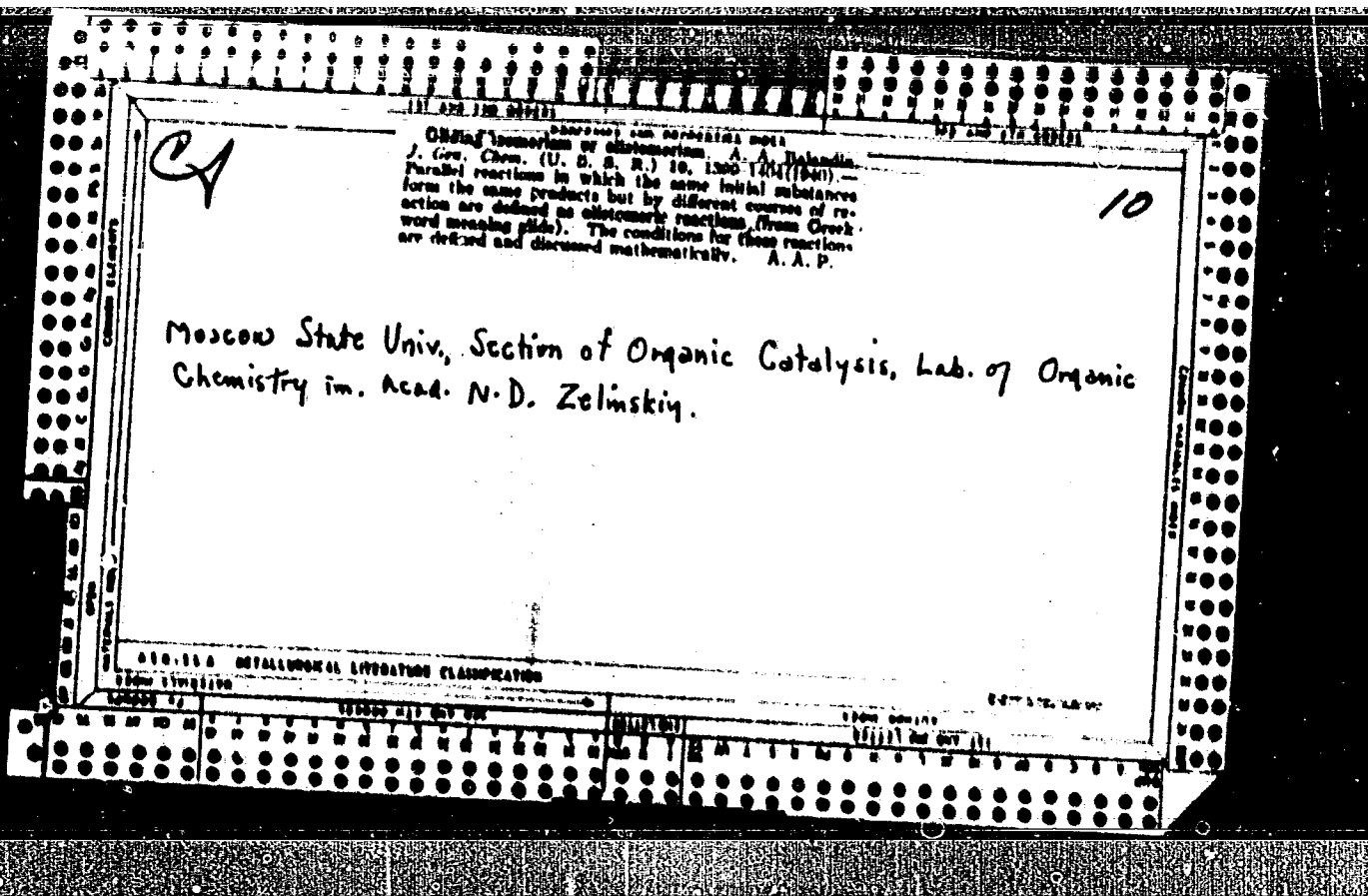












"Reaction of butane with Carbon Dioxide in the Presence of Catalysts, Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 1, 1941.

SALASIN, A. A.

"On the Cleavage of Non-aromatic Ketone by Potassium Permanganate," *Is. Ak. Nauk SSSR,*

Okol. Khim. Ser. B, No. 1, 1961.

БАЛАШИНА, А. А.

"Thermal Decomposition of Rubidium Formate," Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 7,

1941.

"On the Capacity of Metal Formates to be Transformed into Oxalates. Izv. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 2, 1951.

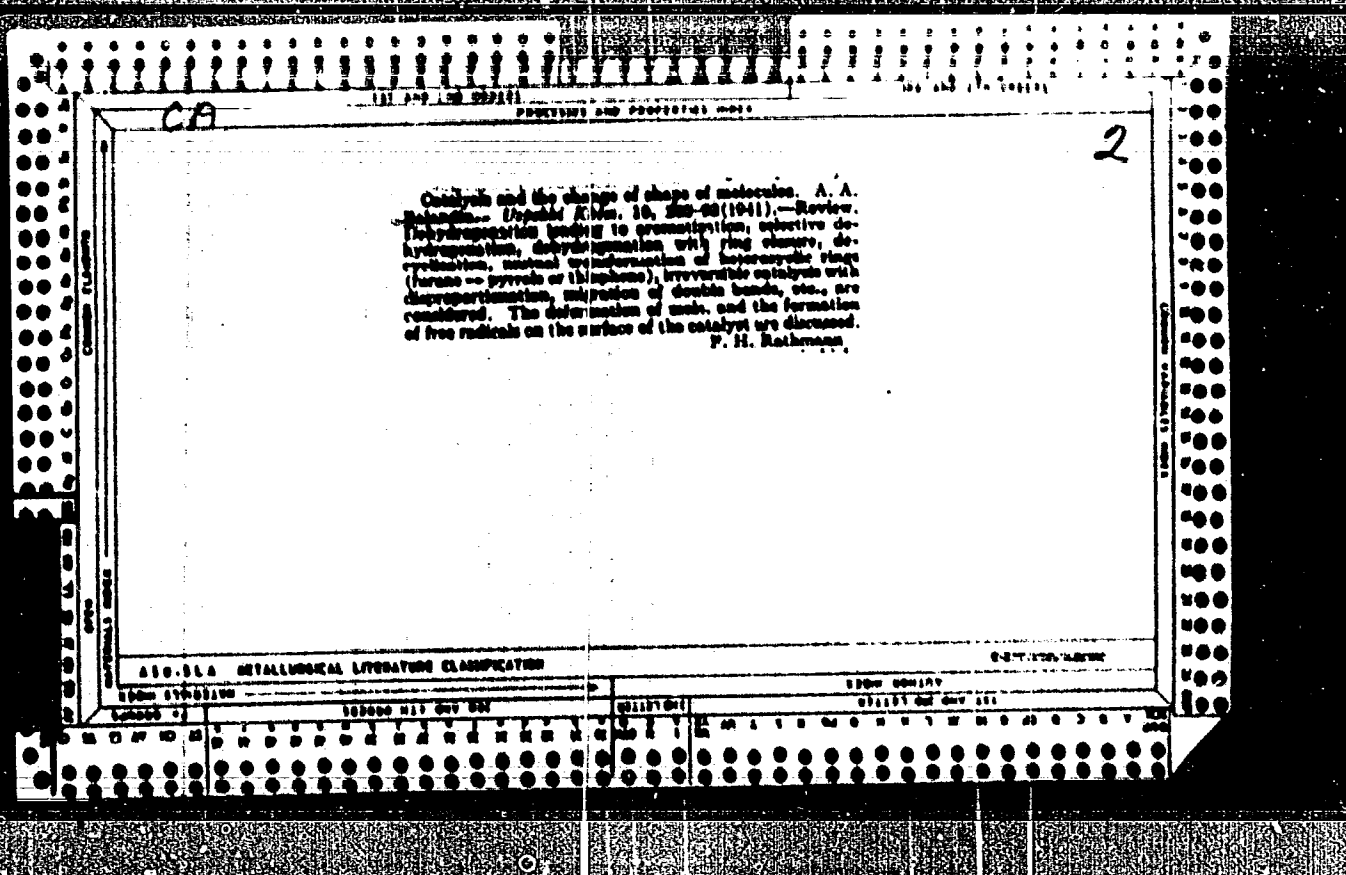
"On the Consecutive Stages of the Thermal Conversion of Formates into Oxalates," Iz. Ak.
Nauk SSSR, Otdel. Khim. Nauk, No. 2, 1941.

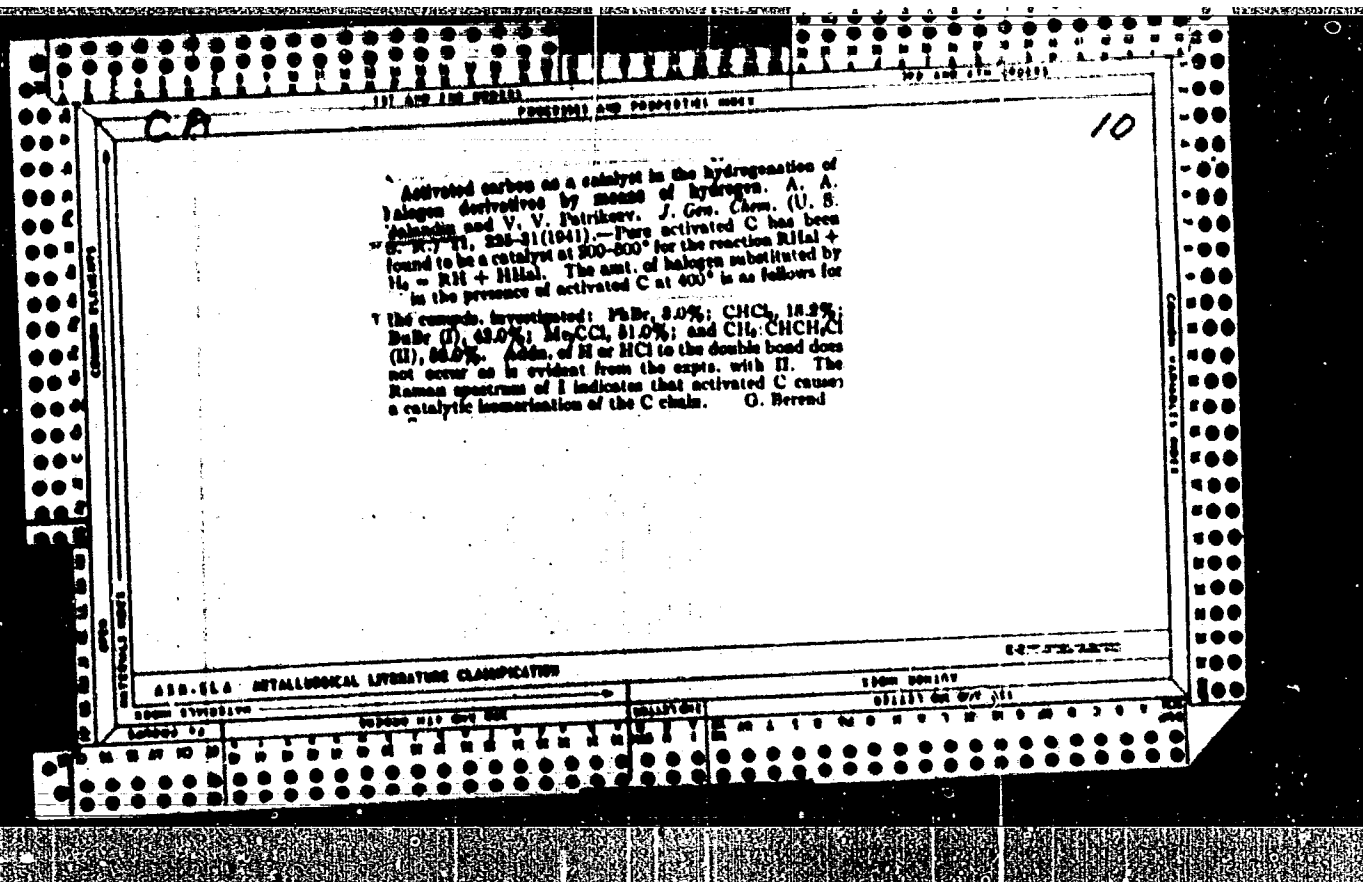
НАУЧНО-ТЕХНИЧЕСКАЯ БИБЛИОТЕКА

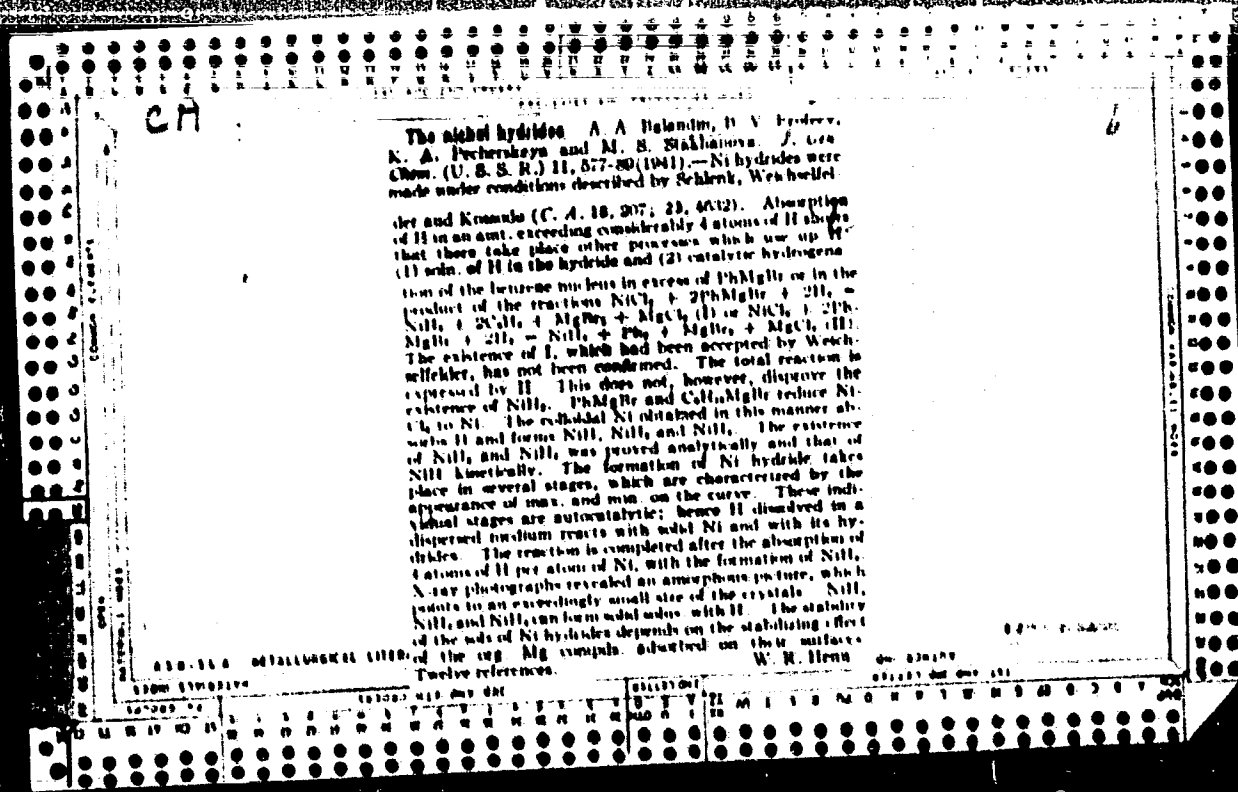
"Thermal Decomposition of Cesium Formate. "Iz. Ak. Nauk SSSR, Otdel. Khim. Nauk, No. 2, 1961.

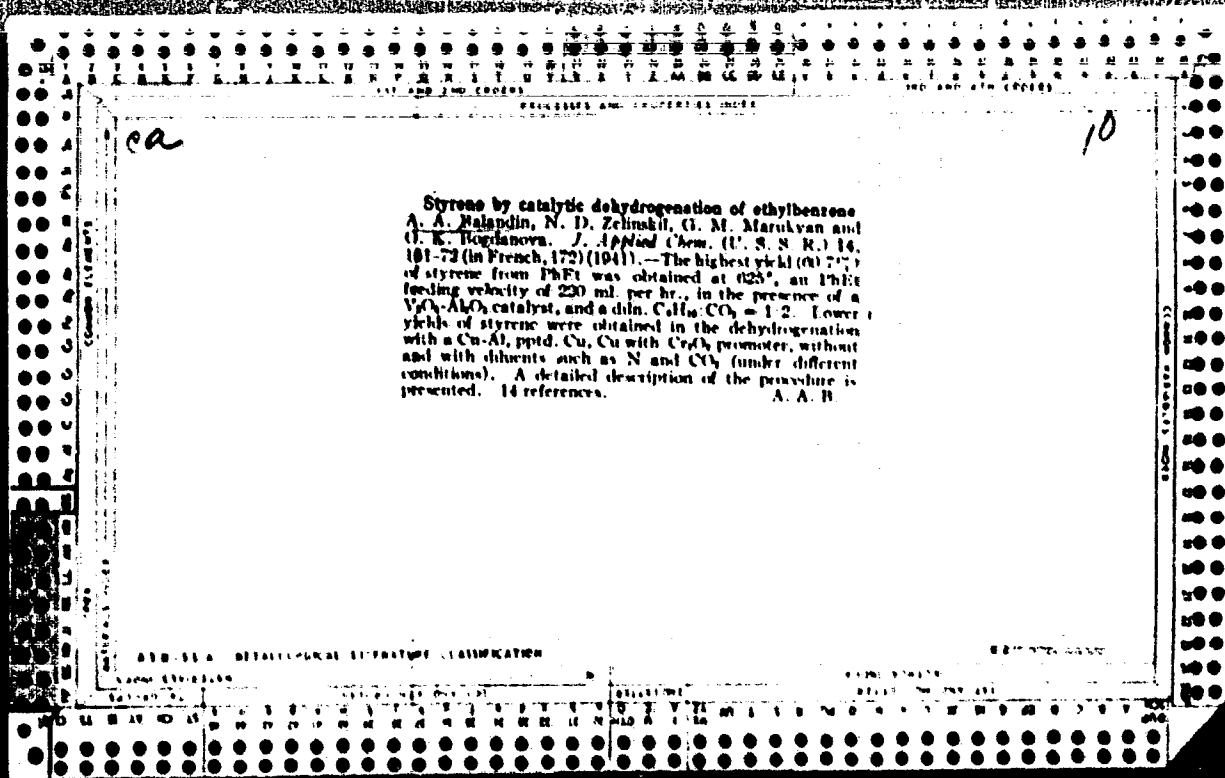
11-10017, 1. 1.

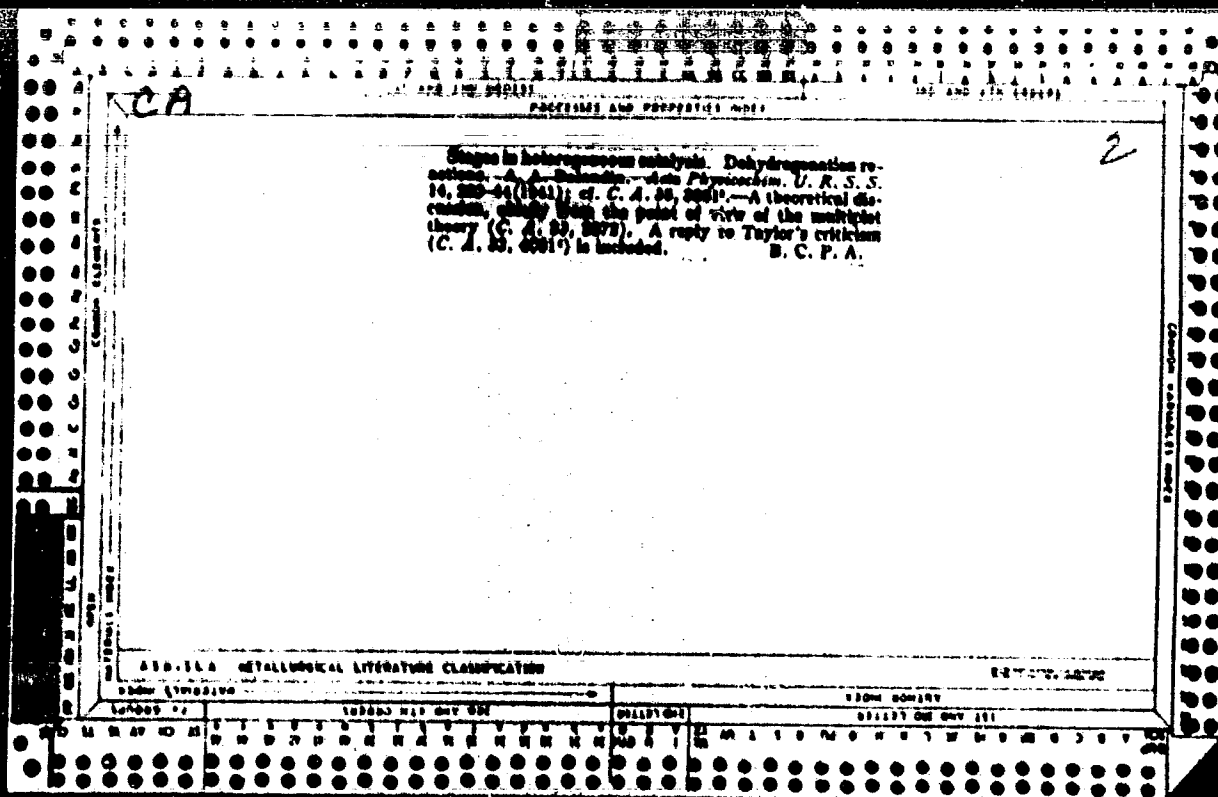
"Thermal Decomposition of Lithium Formate," In: Ak. Nauk SSSR. Otdel. Khim. Nauk, No. 2, 1941.











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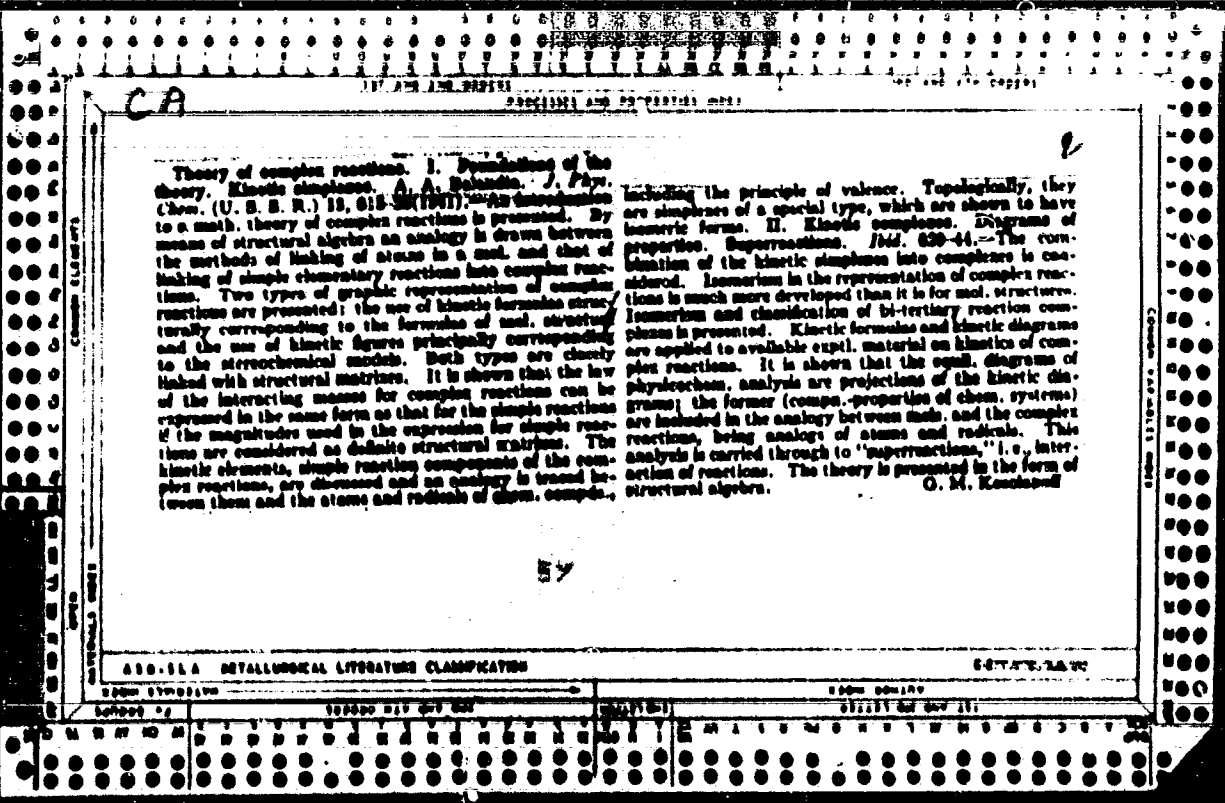
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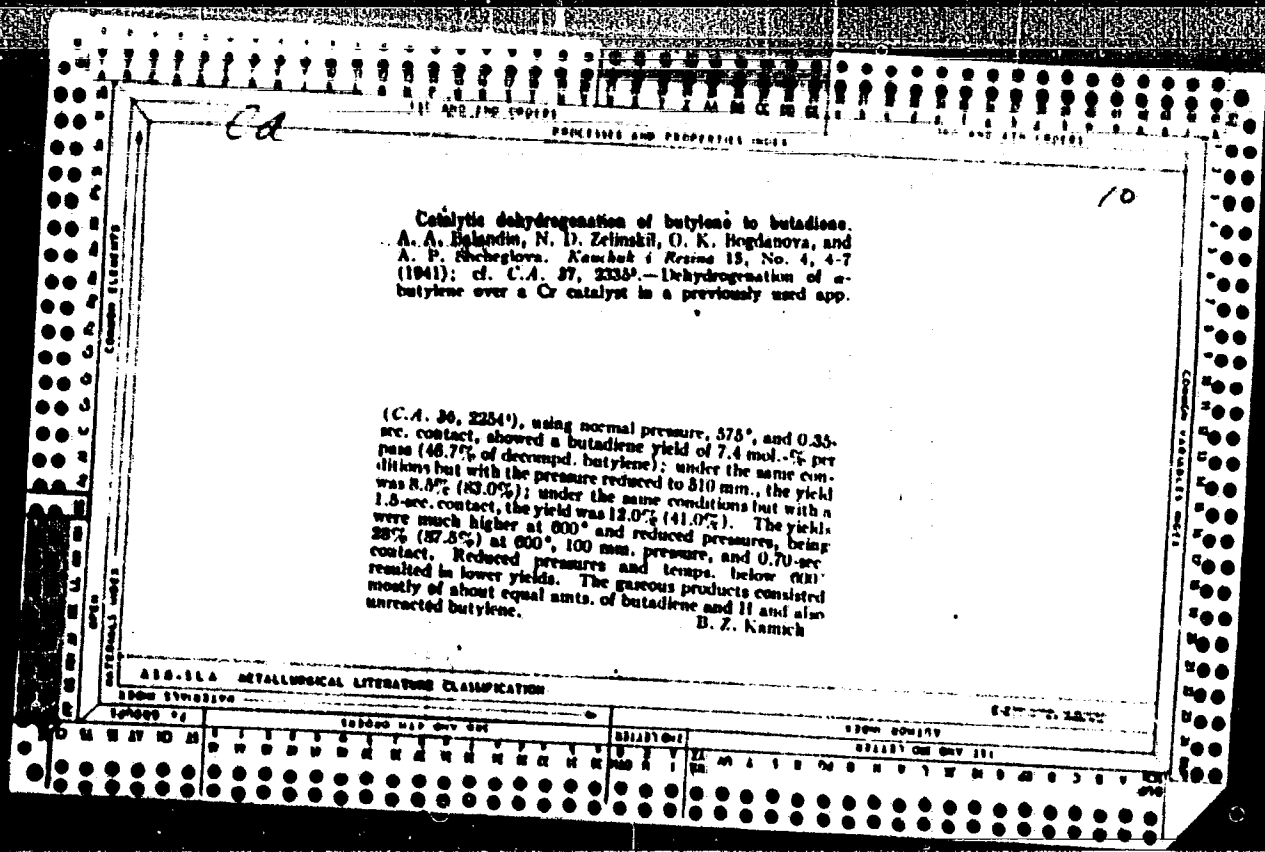
Preparation of divinyl by catalytic dehydrogenation of butene. A. A. Dolandin, N. D. Zelinskii, O. N. Rogdanova and A. P. Shcheglova. *J. Applied Chem. (U. S. S. R.)* 16, 435-45 (in French, 448) (1941); translation in *Foreign Petroleum Tech. J.* 9, 265-82 (1941). - The reaction was carried out in the presence of the following catalysts: Cr₂O₃, Cr₂O₃ on kieselguhr (25% by wt.), Cr₂O₃ and 20% of a mineral closely related to silicon, Cr₂O₃ and CuO (10%), Cr₂O₃ and ZnO (8.1% by wt.), Cr₂O₃ and Mo₂O₃ (80 vol. %), V₂O₅ and Al₂O₃ (20.4% by wt. of V₂O₅), the same obtained by joint spin., Ag₂V₂O₇ (23% by wt.) on kieselguhr (67% by wt.), MgO, and Cr₂O₃ prep. in a special way. The reaction was carried out at atm. pressure while contacting for 0.2 sec. and passing butene in a mist with CO₂ (ratio 1.7.5% by vol.). At 610° the divinyl 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 H₂ and CO in equimol. proportions with a slight admixt. of C₂H₄ and said. hydrocarbons. 10 references. A. A. Hochlingh

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101 102 103 104 105 106 107 108 109 110 111 112 113 114 115 116 117 118 119 120 121 122 123 124 125 126 127 128 129 130 131 132 133 134 135 136 137 138 139 140 141 142 143 144 145 146 147 148 149 150 151 152 153 154 155 156 157 158 159 160 161 162 163 164 165 166 167 168 169 170 171 172 173 174 175 176 177 178 179 180 181 182 183 184 185 186 187 188 189 190 191 192 193 194 195 196 197 198 199 200

PROCESSES AND PROPERTIES INDEX

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Catalytic dehydrogenation of cyclopentane in the presence of chromic anhydride. A. A. Belov and V. B. Fedorov. *Chem. Acad. Sci. U. S. S. R.* 30, 21-2(1941) (in Russian).—Upon heating with Cr₂O₃, 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, 8107), thereby supporting the edge mechanism of the reaction. J. H. Reedy

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

A10-31A METALLURGICAL LITERATURE CLASSIFICATION

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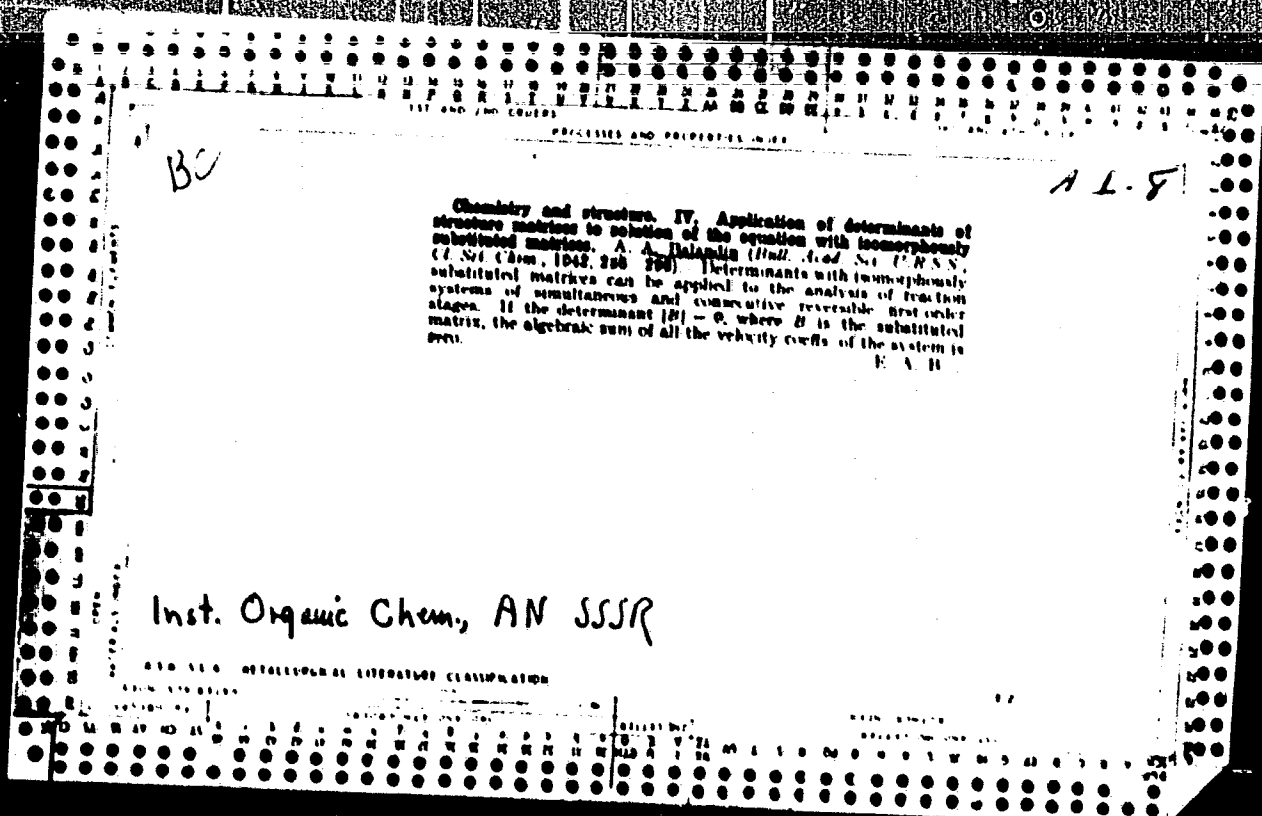
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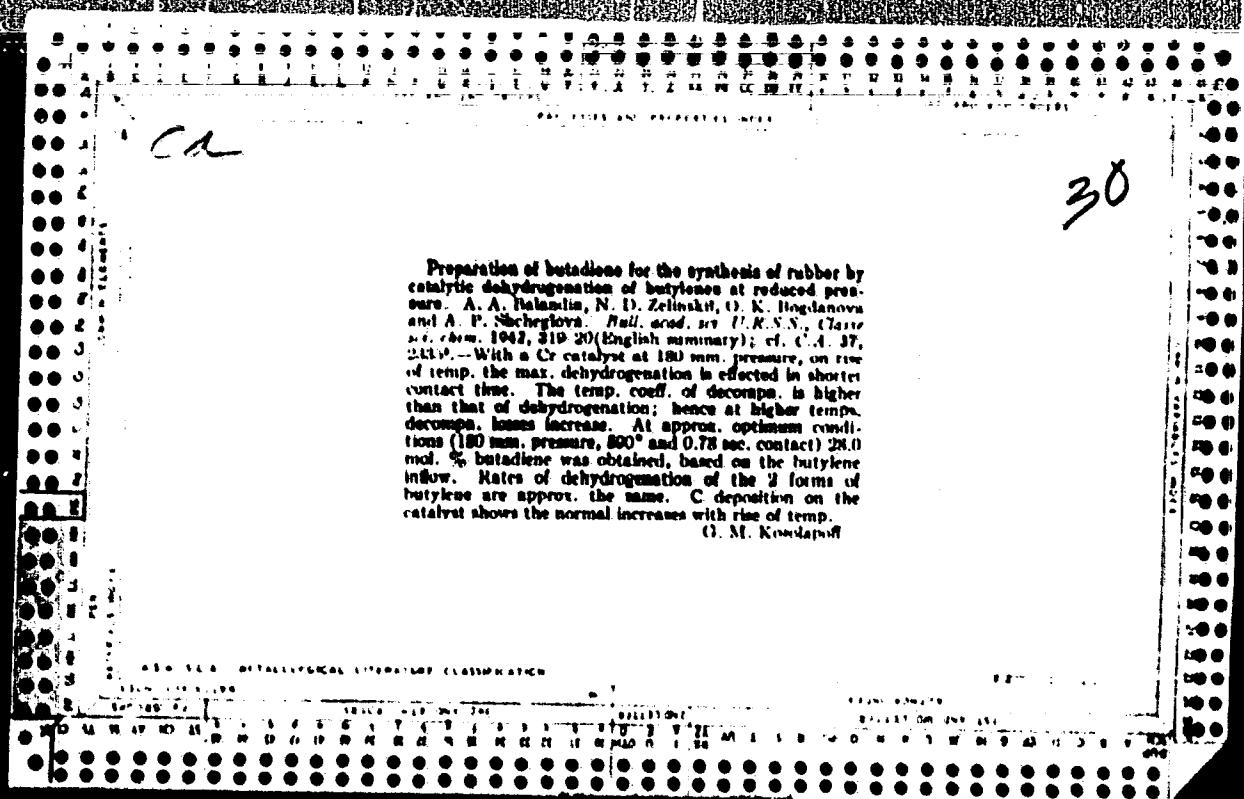
EDMONT STRONG

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_2H_4 , and saturated hydrocarbons obtained from 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 and reactivated by heating in air.

Inst. Org. Chem., AN SSSR





"The Catalytic Dehydrogenation 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

BALABDIN, 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 Erofeev, 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 Waskevitch, D. N. (p. 179)

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

Inst. Organic Chemistry, AN SSSR

BALANOV, 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^1 -Butene (I) passed through an unspecified catalyst gives butadiene; the yield is up to 85% on the (I) consumed and up to 29% on the (I) passed through; the best temp. is 530-600°. The yield of (CH_2CH) 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^2 -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 CH₄ etc. was formed in addition to C₂H₄. Platinised nichrome dehydrogenates (I) at 300-400°; the rate is lowered by dilution with CO₂ at 300-350° and raised by dilution with N₂ at 400°. Soot gradually builds up on the catalyst, and the energy of activation drops from 10 kg.-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 linkages and the mobility of groups and atoms. Isotopes, artificial radioactivity, and optical activity can also be introduced into study of the phenomenon.

A.J.M.

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

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Kinetic study on the dehydrogenation of cyclohexane. A. A. Danilov and F. L. Kostin (*Acta Physicochim. U.R.S.S.*, 1948, 17, 311-317).—The catalytic dehydrogenation of cyclohexane was investigated at 380–430° with Cu on Cr₂O₃ (I), Cu on Cr₂O₃ with BaO (II), and Cr₂O₃ from Cr₂(CrO₄)₃ (III) as catalysts. C₆H₆ is the main product, the yields at 430° being 100% with (I), 13% with (II), and 81% with (III). Contrary to usual results, catalyst (II) did not lose its activity after 80 hr. in use. With increasing temp. the yield of unsaturated hydrocarbons obtained with (II) decreased. Determination of the activation energy and the pre-exponential factor for the reaction show that the sextet mechanism proposed previously (A., 1937, 1, 90) is operative for reaction on catalyst (I). In the other cases the duplet mechanism occurs. J. F. H.

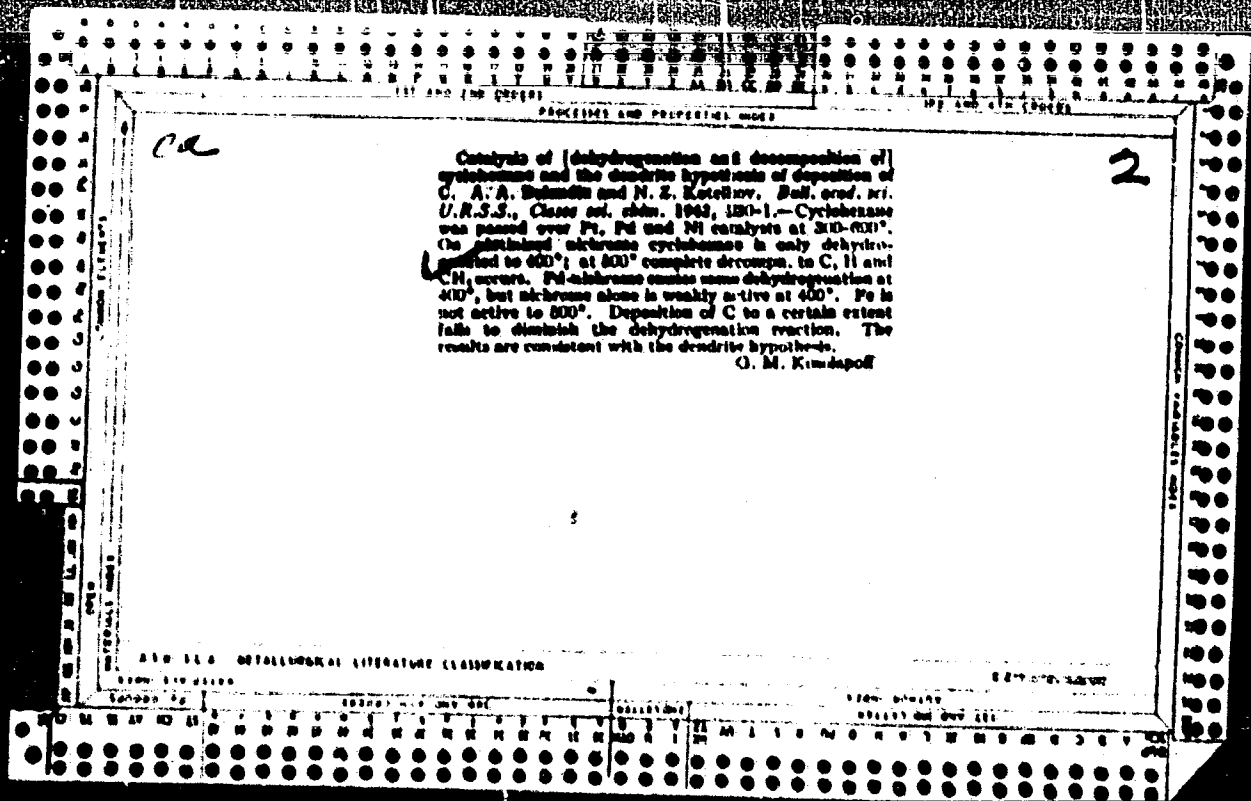
Moscow State U.

Mr. A. S.

A-I-5 - reactions

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

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Carbon deposition in the decomposition of ethylbenzene on metal surfaces and the study of this process by means of a photoelement. A. A. Hologolitskiy and V. V. Patrikeev (Dokl. Akad. Nauk SSSR 1947, 54, 45-48).—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 decamp. of $\text{C}_2\text{H}_5\text{C}_6\text{H}_5$ in presence and in absence of unsaturated hydrocarbons. The reaction has an induction period which decreases with rise of temp. from 450° to 650°; the rate of C formation also increases with temp. J. L. R.

Inst. Organic Chem, AN SSSR

12-26-

Preferential paths in contact catalysis. A. A. Tolstina. *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, 819; 1941, 1, 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. Ha.

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5. 11. 6.
BALANDIN, A. A.

Control decomposition of hydrocarbons. Conversion of *n*-butane under the action of carbon dioxide over nickel-alumina catalysts. A. A. Balandin, M. N. Maruchkin, and M. M. Afanasov (*Acta Physicochim. U.R.S.S.*, 1942, 17, 83-85).—With rise in temp. (θ) from 600° to 800°. [CO] and [H₂] of the product from C₄H₁₀ and CO₂ over a Ni-Al₂O₃ catalyst increase, and the vol. increase tenfold. The hydrocarbon content is all CH₄ at 600° (amount decreasing with θ). For low initial CO₂ content, CH₄ is > original C₄H₁₀, indicating decomp. of C₄H₁₀, and decrease in the C and H content of products indicates decomp. to C. C₂H₄ is found in some experiments but is not due to pyrolysis since no olefins are produced. The results are explained on the multiplet theory (cf. preceding abstract). With the catalyst the C₄H₁₀ first suffers rupture of a primary C-H linkage followed by that of C-C to give H, CH₃, and Pr. H and H recombine to give C₂H₂, and CH₃ with CO₂ gives CO and H₂. The shortened chain repeats the process (calculation shows it to be more favourable). Alternatively CH₃ gives C and H₂ or is hydrogenated to CH₄. CO₂ and PrCHO under similar conditions give olefins (amount increases with θ) as well as paraffins but θ must be higher than with C₄H₁₀. This indicates that PrCHO is not an intermediate in the C₄H₁₀-CO₂ reaction. J. H. Ha.

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Chemistry and structure V The properties of structure determinants Expansion of structure determinants A. A. Belar'in. *Dokl. Akad. Nauk SSSR* (1960, 130, 1042-1044) (English summary); cf. *Ibid.* 1962, 132, 1042, 1044. — Theorems in structural algebra are developed and math. proof is given of the usefulness of structure determinants in detg. chem. structure as proposed by H. M. Leussink. (C. A. 34, 7671)

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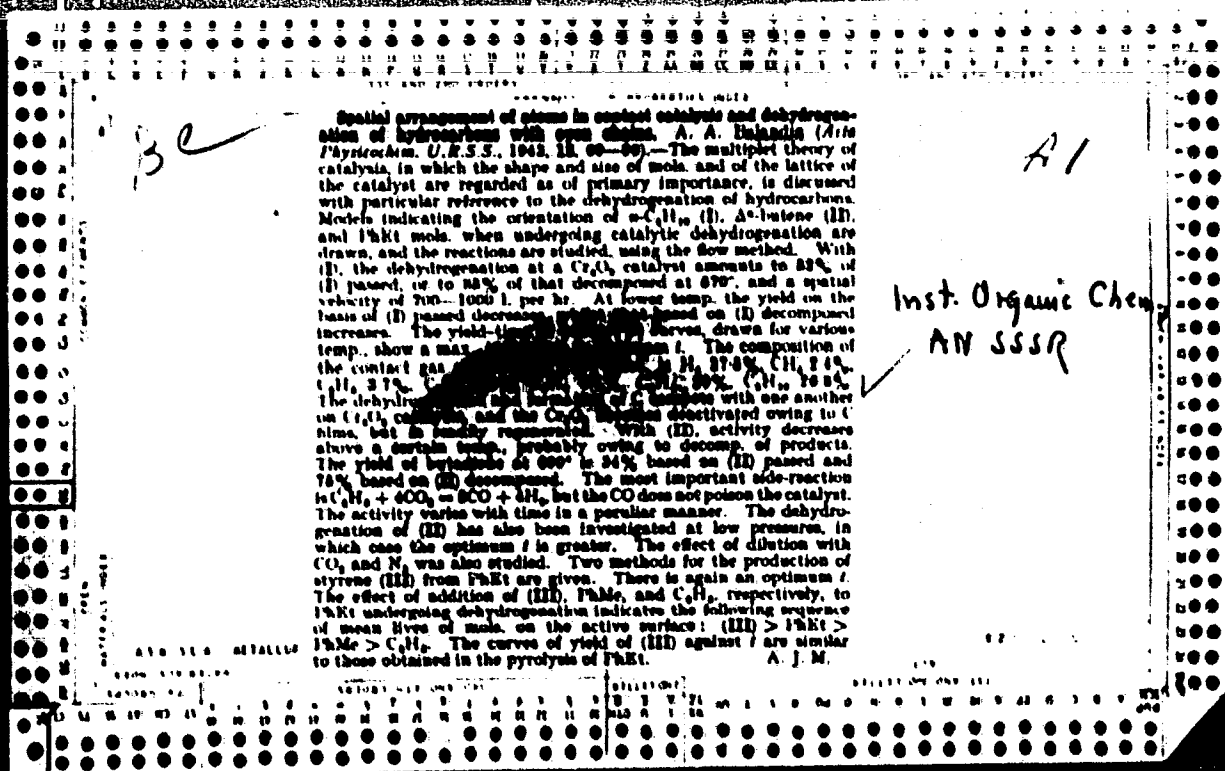
A 18, Reactions

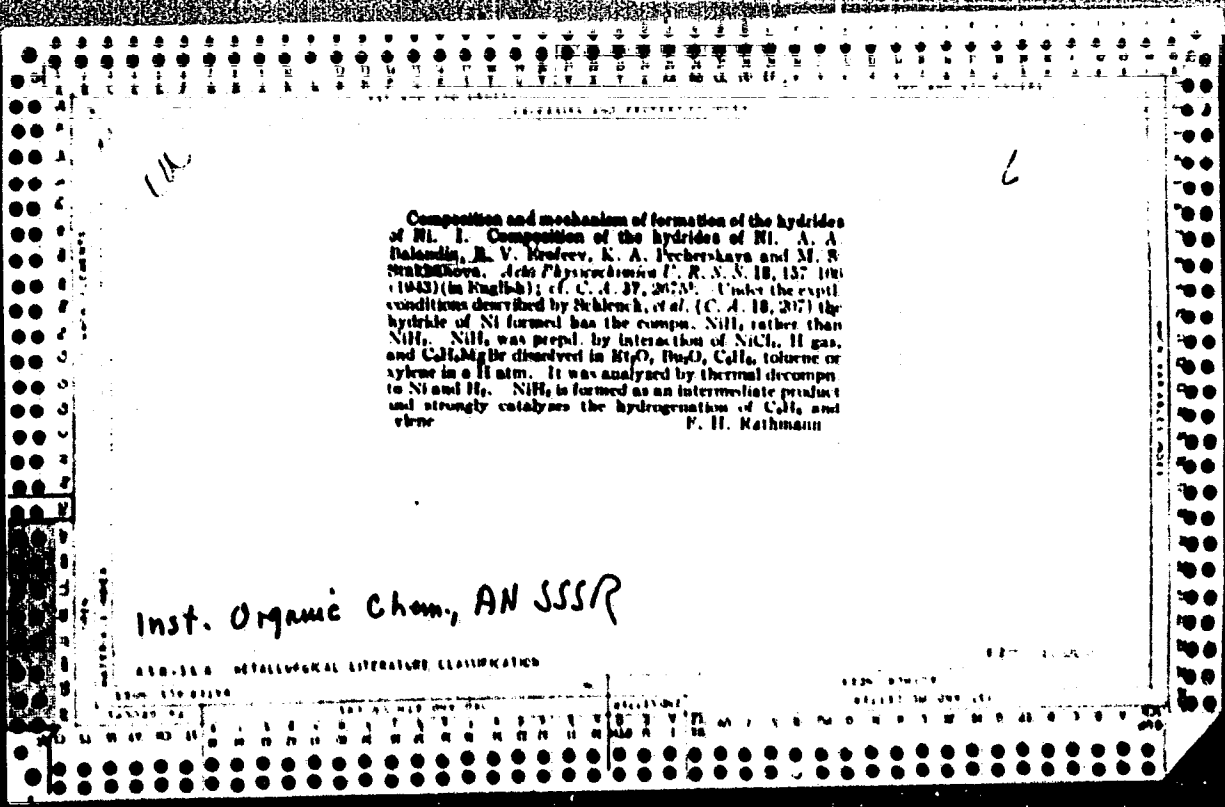
Thermal study of catalytic reactions by means of the differential thermocouple. A. A. Bolandin and V. V. Patrikeev (*Dokl. Akad. Sci. U.R.S.S., Chem. Sect.*, 1943, 476-477). Information as to the course of a catalytic reaction may be obtained by a thermocouple, one junction of which is in the catalyst and the other in similar, but inert, material placed adjacent to it. V. H.

7-7

Selective hydrogenation. A. A. Bolandin (Bull. Acad. Sci. U.S.S.R., Ch. Sci. Chem., 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. H.

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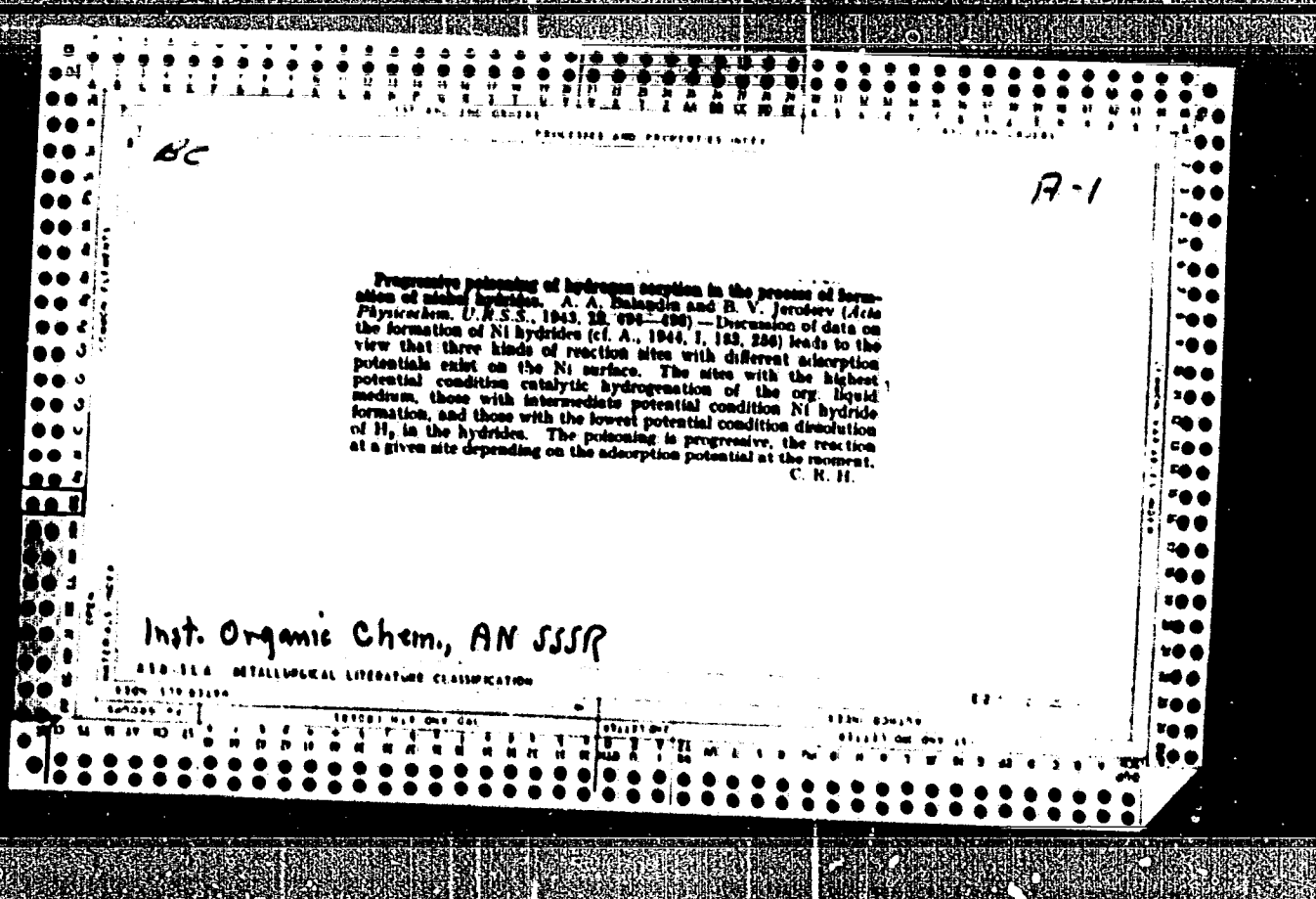


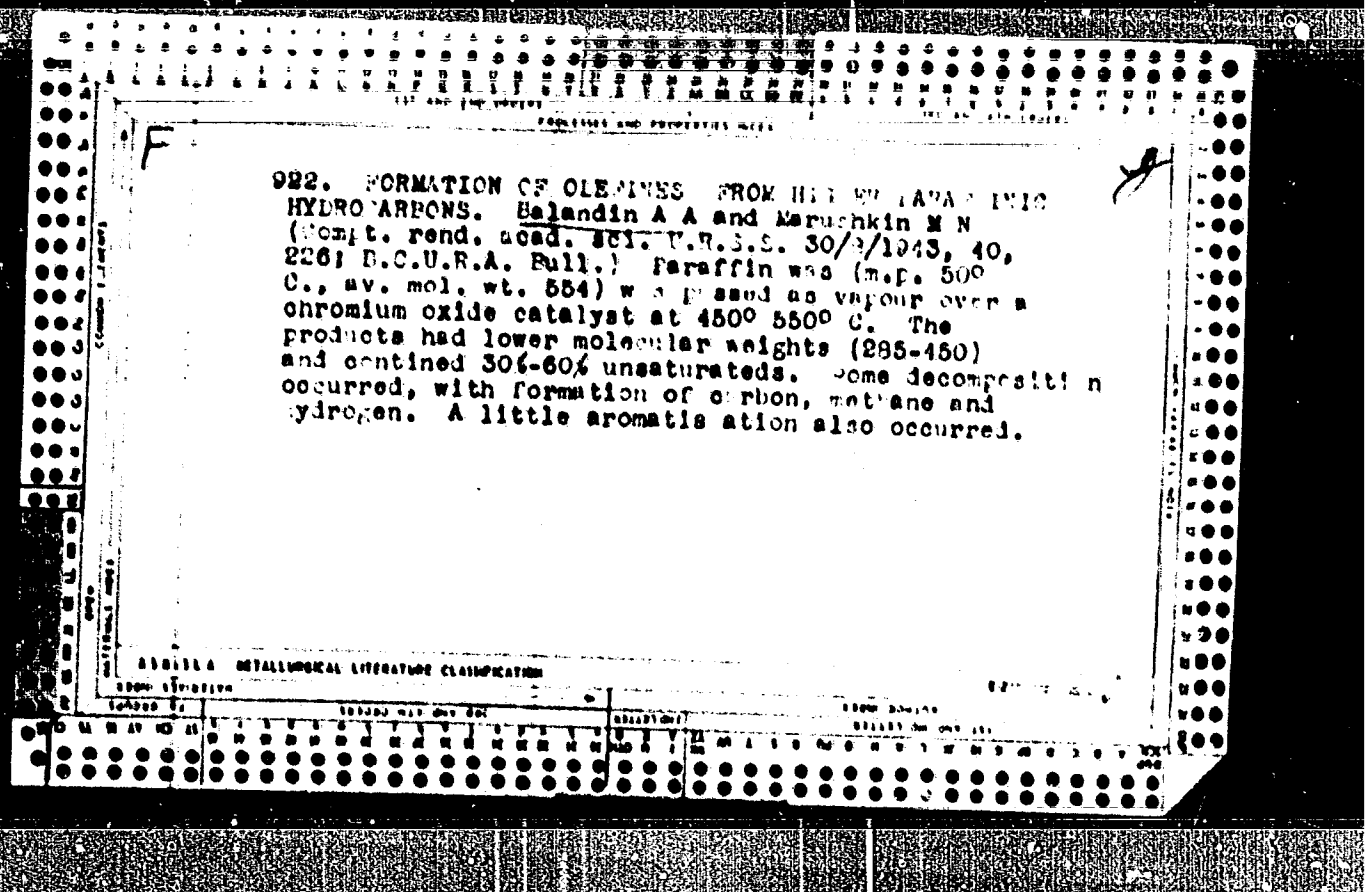
Composition and mechanism of formation of the hydrides of nickel.
II. Reaction mechanism. A. A. Italandin, B. V. Jersolov, K. A. Ivchinskaja, and M. S. Stachivkova *Vysokomol. Soedin. USSR Phys. Chem. USSR*, 1973, 15, 300-310. Wechselschler's view that the formation of NiH_2 from NiCl_2 , Mg^{2+} , and H_2 is due to the interaction of H_2 with Ni^{2+} , formed as an intermediate compound, is incorrect. NiCl_2 is reduced to Ni by Mg^{2+} 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_3 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. Solids of Ni hydrides in Et_2O and other solvents were examined. Those in Et_2O are less stable than those in C_6H_6 , Et_2Me , and xylene. Colloidal solutions in Et_2O are formed only when $[\text{Mg}^{2+}]$ is $> 0.5M$, suggesting that adsorption of Mg^{2+} on the hydride surface protects the colloid. H_2O and air rapidly coagulate the sol. C. R. H.

Dendritic hypothesis of carbon deposition. Chemical behaviour of carbonaceous when in contact with electrically heated metallic cath. A. Italandis and N. Kotelnov (*Acta Physicochim. U.R.S.S.*, 1943, 18, 406-418).—The catalytic dehydrogenation and decomp. of cyclohexane over Pt- and Ni-nichrome and decomp. of at 300-400° 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 is the form of dendrites is suggested in explanation. C. R. H.

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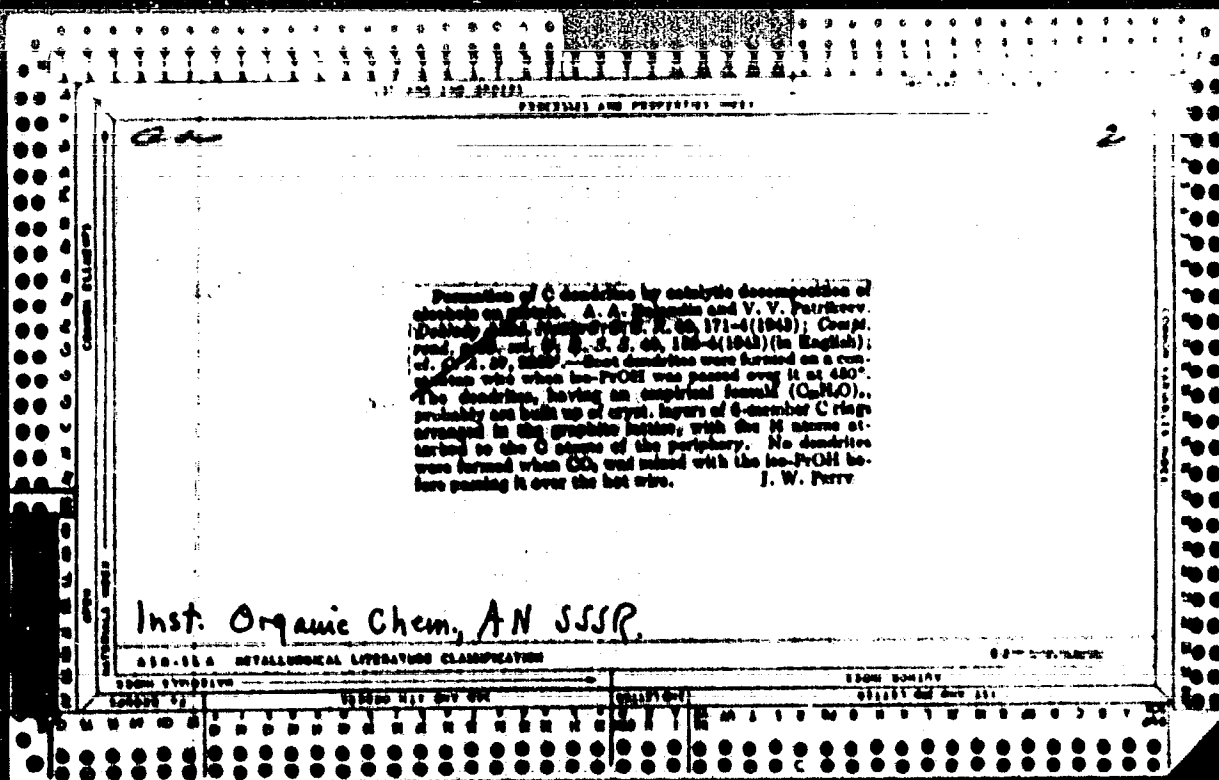


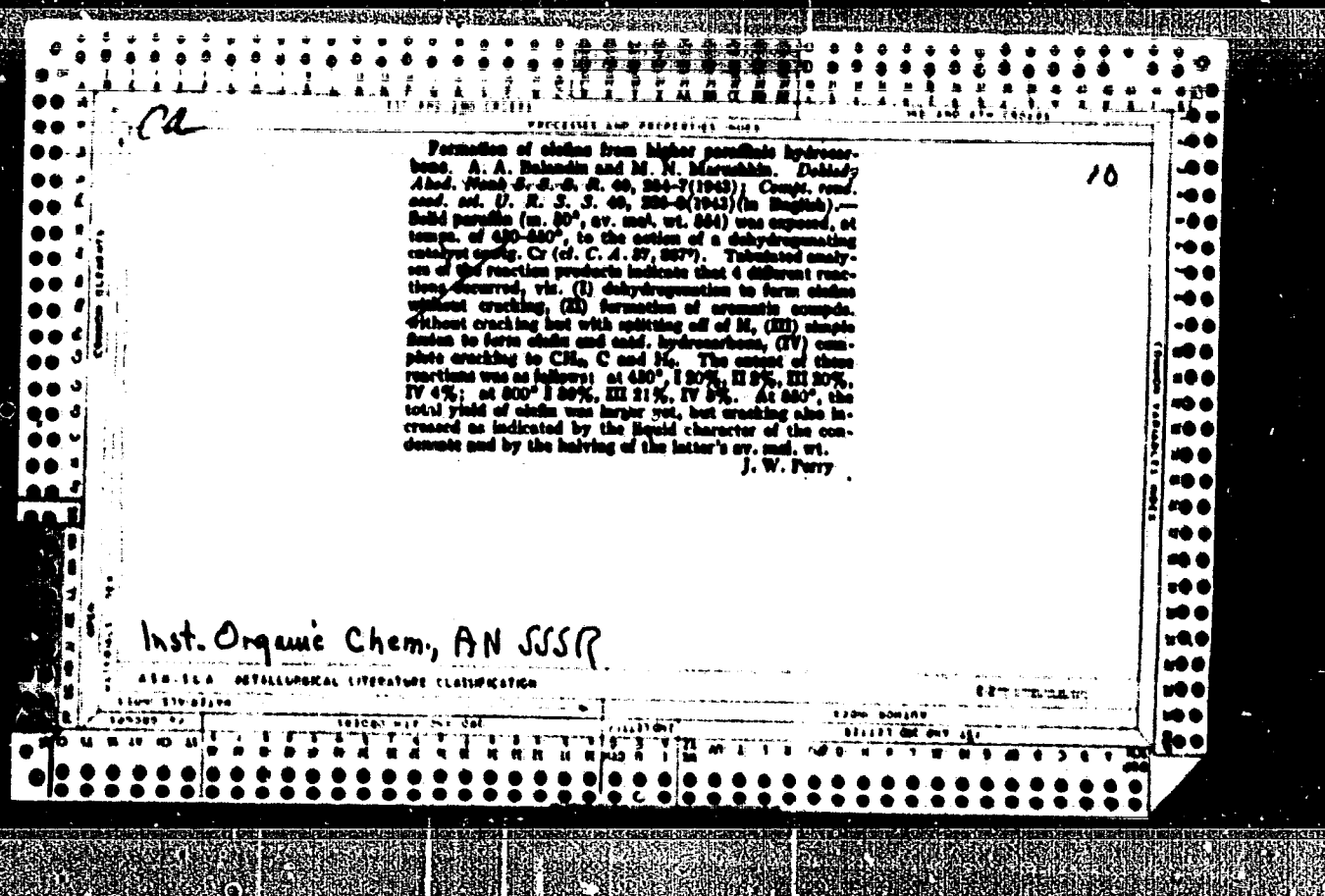


Kinetics of consecutive reactions consisting of bimolecular and unimolecular stages. A. A. Galanin and L. S. Leibson (Compt. rend. Acad. Sci. U. R. S. S., 1963, 39, 22-24).--The equations for consecutive reactions of the type $2A+B \rightarrow C$ are solved, and the results compared with experiment in 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.

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Catalytic dehydrogenation of *p*-cymene. A. A. Mal'nev (i. M. Muzhyn and N. G. Shtromovsk. *Doklady Akad. Nauk S. S. R.* 41, 71-3(1943); *Compt. rend. acad. sci. U. R. S. S.* 41, 67-9(1943)(in English).—Con-

version of *p*-cymene (I) into *o*,4-dimethylstyrene (II) can be carried out efficiently by using catalysts and conditions previously worked out for conversion of StPh into styrene (cf. C. A. 36, 417^o). Optimum conversion of I into II amounted to 63.4% when 3 mole. CO₂ were admitted per mole. I before passing over the catalyst, which retained its activity after use for 81 hrs. Without CO₂, the best conversion of I was 29.3%. Supplementary expts. showed that II can be polymerized by heat, cold, concd. H₂SO₄, or NaOH. J. W. Perry

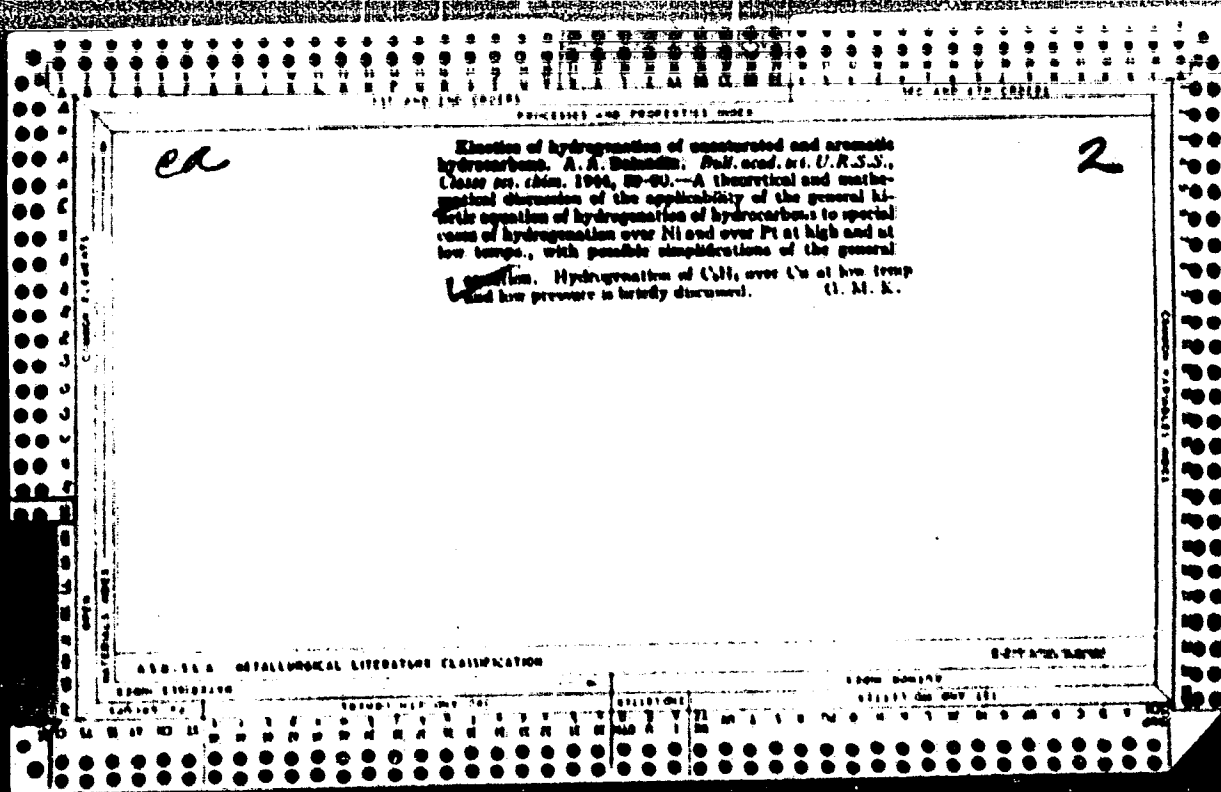
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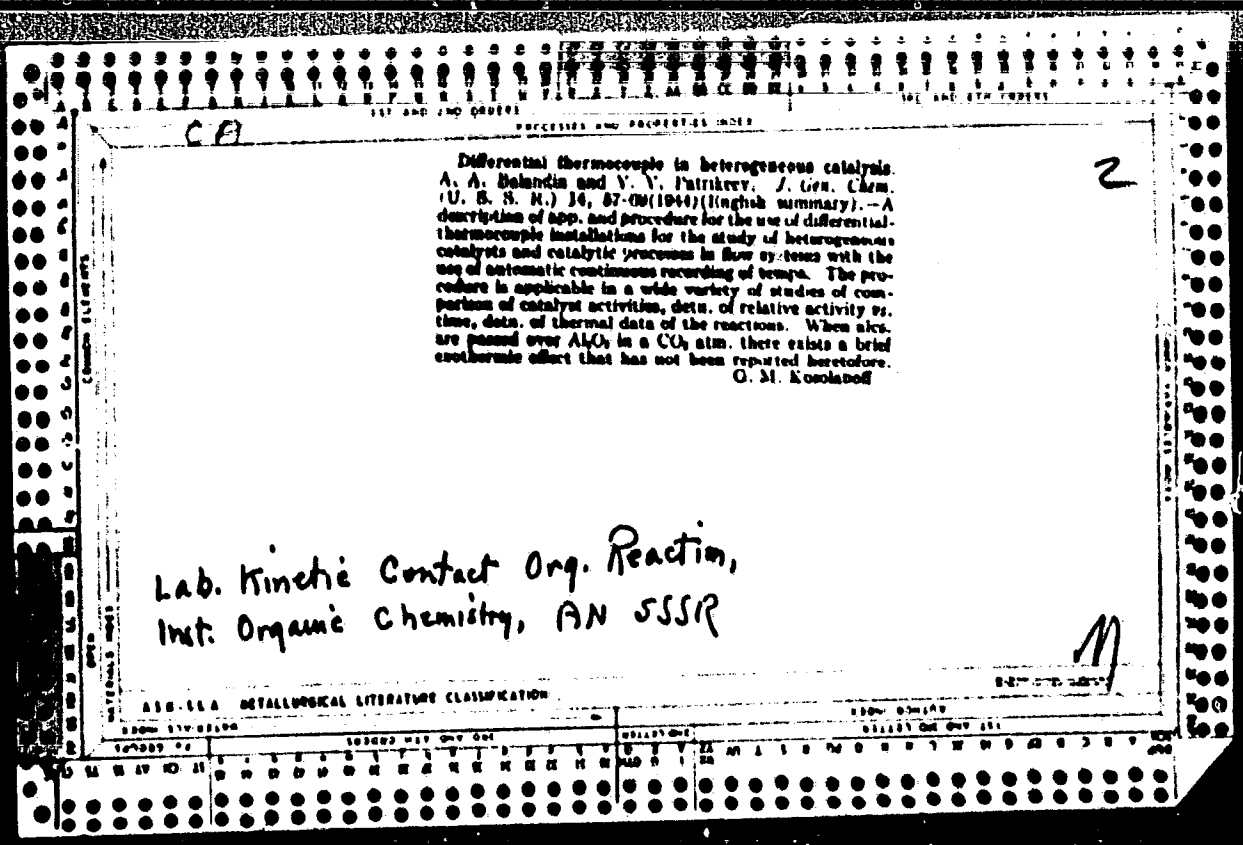
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Dehydrogenation of EtOH over mixed catalysts. B. L. Leitch, A. A. Balandin, D. N. Vashkevich and I. J. Ozer. *J. Applied Chem. (U. S. S. R.)* 17, 90-4(1944) (Russian summary).—Using 3-component catalysts of Cu-Al₂O₃ promoted by Cd or Ti oxides EtOH was dehydrogenated with the formation of considerable amts. of AcOH and EtOAc. The Cd-promoted catalyst has no advantage over the Cu-Al₂O₃ catalyst, while TiO₂ promoter favors the EtOAc formation: at 300 cc. per l. catalyst volume rate at 295° there may be obtained per pass up to 23.7% EtOAc and 19% AcOH. The formation of EtOAc on the TiO₂-promoted catalyst has a lower activation energy (2770 cal./mol.) than on the Cd-promoted catalyst (14,800 cal./mol.). O. N. Kozlovskii

Alkyl 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, 143-60(1945); cf. *C. A. B.* 39:297.—Butenylmagnesium bromide (I) (Part XV) and HCl in ether give octadecenes (bp 65-108°) and 80% of 2-methyl-2-buten-1-ol (II), bp 120-1°. n_D²⁰ 1.4301; 2,2-dimethyl-2-buten-1-ol, m. 57.5-6°; the structure of II follows from the action of O₂, which gives HCHO, and reduction to 2-methyl-1-butanol. I and Me₂CO give 81% of 2,2-dimethyl-2-pentan-2-ol, bp 94.5-95°, n_D²⁰ 1.4266; 2,2-dimethyl-2-pentan-2-ol, m. 78-8.5°. I and AcCl give 94% of 2-methyl-2-pentan-2-ol, bp 128-9°, n_D²⁰ 1.4315; 2,2-dimethyl-2-pentan-2-ol, m. 44-4.5°; hydrogenation gives 2-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)CH₂CH₂) and not RCH:CHCH₂MgX. Carbonylation of the Grignard reagent from CH₂C=CH(OH)Me gives 70% of CH₂:CH-CHMeCO₂H; dibutenylmagnesium gives 37% of the same acid. Thus, the equl. in the Grignard soln. of the type 2RMgX ↔ R₂Mg + MgX₂ 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

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PROCESSES AND PROPERTIES INDEX

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Anisochromism and its experimental determination.
 A. A. Bahadur. *Acta Physicochim. U.R.S.S.* 19, 313-323 (1948) (in English).--Math. and theoretical. The anisochromism of the mixtures *A* and *B* is defined as a quantity that shows, as a ratio, how much longer a unit of *A* remains in the adsorbed state on the active surface of a catalyst than does a unit of *B*. On the basis of equations developed previously (C.A. 39, 4612) 3 methods, one simplified and one exact, are developed for detg. the mean lifetimes of units on the active surface and hence for detg. the anisochromism. 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 anisochromism.
 T. H. Denckler

Inct. Org. Chem., AN SSSR

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"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.

