SHILOV, V.N.; BELIKOVA, N.N.; YERSHOVA, Z.P.

Fusion method for approximating the chemical composition of Cenozo igneous rocks in South Sakhalin. Dokl. AN SSSR 119 no.2:326-329 Mr '58. (MIRA 11:5)

1. Sakhalinskiy kompleksnyy nauchno-issledovatel'skiy institut AN SSSR. Predstavleno akademikom D.S. Korzhinskim.
(Sakhalin--Rocks, Igneous)

3(0) SOV/20-122-5-43/56

AUTHORS: Shilov, V. N., Kalishevich, O. K.

TITLE: The Problem of the Genesis of Spilite-Keratophyre (K voprosu ob usloviyakh obrazovaniya porod spilito-keratofirovoy formatsii)

PERIODICAL: Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 5, pp 902-904 (USSR)

ABSTRACT: The spilite-keratophyre formation (the zelenokamennaya greenstone formation) is typical of geosynclines. Such rocks usually originate in the beginning of the geosynclinal cycle (Ref 2). According to present ideas (Ref 1), the spilitic formations, although occurring with differing acidities, are built over a long period of time under submarine conditions. It is just these conditions and not the original compositions that are held responsible for the peculiar end-composition (markedly differing from the usual calc-alkali series) of the spilite lavas. The paleogeography of Sakhalin during the Tertiary was often favorable for the formation of spilite-keratophyre (Early and Middle Miocene, Ref 3, Late Neogene, Early Pliocene). An analysis of fauna remains in these formations allows not only

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The Problem of the Genesis of Spilite-Keratophyre SOV/20-122-3-43/56

the exact determination of the time of volcanic activity, but also the determination of the paleoenvironment. Especially the depth of the water in which single eruptions took place. Mrs. T. C. Kaltshevich on the basis of the fossil associations and the lithology concluded that the pillow lavas and ball lavas (of the Vyazovka River and Cape Staritskogo) erupted at a depth of approximately 50-60 m under normal conditions of salinity and gas exchange. On the other hand the analogous lavas on the north point of Cape Lamanon erupted in the litteral zone, at depths of less than 15-20 m. Due to the rapid cooling the lavas are quite glassy with a microporphyritic texture. Although the extrusion under the water has produced a special texture and also to some extent influenced the mineral composition, the plagioclase is in no way albitized - the particular characteristic of spilite-keratophyre. This study has shown that submarine eruption alone, at least up to depths of 100 m, is not enough to produce spilite lavas. There are 1 table and 6 references, 4 of which are Soviet.

ASSOCIATION: Sakhalinskiy kompleksnyy nauchno-issledovatel'skiy institut Akademii nauk SSSR (Sakhalin Scientific Research Institute of

Card 2/3

SHILOV, V.N.; ZAKHAROVA, M.A.; IL'YEV, A.Ya.; PODZOROV, A.V.

Eruption of the Yuzhno-Sakhalinsk Mud Volcano in the spring of 1959.
Trudy Sakh.kompl.nauch.-issl. inst. AN SSSR no.10:83-99 '61.
(MIRA 15:6)

(Sakhalin--Volcanoes)

FEDORCHENKO, V.I.; SHILOV, V.N.

Eruption of the Chikurachki Volcano (Paramushir Island) in 1961. Biul. Vulk. sta. no.34:36-43 '63. (MIRA 16:10)

KIRSANOV, I.T.; SERAFIMOVA, Ye.K.; SIDOROV, S.S.; TRUBENKO, V.F.;
FARBEROV, A.I.; FEDORCHENKO, V.A.; SHILOV, V.N.

Eruption of the Ebeko Volcano from March to April, 1963.
Biul. vulk. sta. no.36:66-72 '64. (MIRA 17:9)

SHILOV, V.N.; IL'YEV, A.Ya.; PODZOROV, A.V.

Eruption in Sakhalin. Priroda 54 no.8:95-96 Ag '65. (MIRA 18:8)

1. Sakhalinskiy kompleksnyy nauchno-issledovatel'skiy institut Sibirskogo otdeleniya AN SSSR, poselok Novo-Aleksandrovsk.

15-57-4-4306

Study of the Paleolithic in the Lower Don Region (Cont.)

regions, where discoveries of Neanderthal culture are already well known. The lower Don region is apparently also a promising region for searching for lower Paleolithic sites.

Card 2/2

SHILOV, V. P.

15(0),15(2)

AUTHOR: Kolomiyets, B. T., Doctor of Technical Sciences SOV/30-59-2-45/60

TITLE: The Investigation of Vitreous Semi-Conductors (Izucheniye stekloobraznykh poluprovodnikov)

PERIODICAL: Vestnik Akademii nauk SSSR, 1959, Nr 2, pp 103-104 (USSR)

ABSTRACT: From December 1 to 2, 1958 a conference took place on this problem at the Fiziko-tekhnicheskiy institut Akademii nauk SSSR (Physicotechnical Institute of the Academy of Sciences, USSR). It dealt with the discussion of the experiments carried out, mutual information on the course of experiments and their general coordination. Representatives from 11 scientific institutions attended the conference. The following lectures were heard: V. V. Tarasov, Moskovskiy khimiko-tekhnologicheskiy institut (Moscow Chemicotechnological Institute) spoke of experimental results connected with the investigation of heat capacity at low temperatures of As_2S_3 and As_2Se_3. His second report dealt with the polymeric concept of glass formation and semiconductors in general.

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R. L. Myuller, Gosudarstvennyy opticheskiy institut (State Optical Institute) emphasized the decisive role played by the covalent bond in glass formation.

A. A. Vaypolin, Institut khimii silikatov Akademii nauk SSSR (Institute of Silicate Chemistry of the AS USSR) described the investigation of the structure of the system As_2Se_3-As_2Te_3 by X-ray methods.

L. I. Tatarinova, Institut kristallografii Akademii nauk SSSR (Crystallographical Institute of the AS USSR) reported on the structural investigation of some chalcogenids by electron-diffraction.

A. I. Gubanov and V. Ya. Khartsiyev, Fiziko-tekhnicheskiy Institut (Physicotechnical Institute) reported on theoretical problems of the semiconductor properties of glass types.

V. P. Shilo discussed working results in the determination of boundaries in glass formation in the As_2S_3 and As_2Se_3 systems.

N. A. Goryunova compared the boundaries of vitreous state in these systems with the criteria of glass formation obtained by Zakhariasen and Vinter-Kleyn and found that there exists no correlation between them.

T. F. Nazarova investigated the electric properties of semiconductor glass types in the TlSe - As_2Se_3 system.

B. T. Kolomiyets spoke of research work in the field of inner photoelectric effect done by T. N. Mamontova.

B. V. Pavlov discussed experimental results of the position of the absorption boundary as dependent on the change of composition of glass types.

V. P. Posdnev reported on material he obtained in the investigation of the viscosity of glass types in the As_2Se_3 - As_2Te_3 system.

B. T. Kolomiyets summarized the working results obtained by the Physicotechnical Institute and found that in the materials investigated the short-range order is not changed in the transition from the vitreous into the crystalline state.

O. V. Mazurin, Leningradskiy khimiko-tekhnologicheskiy institut (Leningrad Chemicotechnical Institute) described the investigation of the semiconductor properties of silicate and borosilicate glass types with the addition of iron-cobalt and titanium oxides.

N. V. Petrovykh, Moskovskiy institut elektrotekhnicheskogo stekla (Moscow Institute of Electrotechnical Glass) outlined the investigation results of the boundaries of glass formation and the electric properties of contiguous semiconductor glass types of the composition V_2O_5 - P_2O_5 - R_xO_y (R- elements of the I, II, III, IV and V groups of the periodic system).

The next conference on semi-conductor glass types will probably be held in 1959.

6

VASHKO, A.; PROKOPOVA, G.; KOLOMIYETS, B.T.; PAVLOV, B.V.; SHILOV, V.P.

Absorption spectra of glass of the system As_2S_3--$As_2 Se_3$. (MIRA 15:2)
Opt. i spektr. 12 no.2:275-277 F '62.
(Arsenic sulfide--Spectra)
(Arsenic selenide--Spectra)

Effect of disturbance of short-range order on the electrical properties of solid solutions with tetrahedral structure of distribution of atoms. D. I. Tret'yakov.

Some electrical properties of solid solutions in the system $AgInTe_2$-2InSb. S. M. Mamayev, V. D. Prochukhan. (Presented by D. I. Tret'yakov--15 minutes).

(Paper not presented).]

Investigation of thermally stimulated current in vitreous $Tl_2Se \cdot As_2Te_3$. A. M. Andriyash, B. T. Kolomiyets.

Measurement of the mobility of current carriers in vitreous chalcogenide semiconductors. I. B. Ivkin, B. T. Kolomiyets, E. A. Lebedev.

Oxychalcogenide Glasses. B. T. Kolomiyets, V. P. Shilo. (Presented by B. T. Kolomiyets--20 minutes).

Report presented at the 3rd National Conference on Semiconductor Compounds, Kishinev, 16-21 Sept 1963

PHASE I BOOK EXPLOITATION 540

Shilov, V.S.

Ratsional'nyye konstruktsii shtampov kholodnoy shtampovki; opyt Leningradskogo zavoda "Krasnaya zarya" (Efficient Die Design for Cold Working; Practices of the "Krasnaya Zarya" Plant in Leningrad) Leningrad, 1955. 14 p. (Leningradskiy dom nauchno-tekhnicheskoy propagandy. Informatsionno-tekhnicheskiy listok, no. 88 /776/) 7,000 copies printed.

Sponsoring Agencies: Leningradskiy dom nauchno-tekhnicheskoy propagandy, and Vsesoyuznoye obshchestvo po rasprostraneniyu politicheskikh i nauchnykh znaniy.

Ed.: Chuloshnikova, Ye.P., Engineer; Tech. Ed.: Freger, D.P.

PURPOSE: This pamphlet contains a brief description of various dies and of the elements of die design. It may be of interest to diemakers and to apprentices in this trade.

Card 1/3

Efficient Die Design (Cont.) 540

AVAILABLE: Library of Congress

Card 3/3

GO/ad
8-25/58

GOROKHOVSKIY, A.I.; ZINYUK, M.N.; SHARDAKOV, S.V.; SHILOV, V.S.

Semi-automatic distribution conveyer. Kozh.-obuv.prom.
no.10:9-12, O '59. (MIRA 13:2)
(Assembly-line methods) (Shoe manufacture)

VAYNTRAUB, David Abramovich; KUZNETSOV, Dmitriy Petrovich; FILINA, Irina Stepanovna; SHILOV, Viktor Stepanovich; TSUKKER, G.Ye., red.; FREGER, D.P., red. izd-va

[Cold extrusion] Kholodnoe vydavlivanie; obzor. Leningrad. No.1. 1961. 62 p. (MIRA 15:4)

(Extrusion (Metals))

VAYNTRAUB, David Abramovich; KUZNETSOV, Dmitriy Petrovich; FILINA,
Irina Stepanovna; SHILOV, Viktor Stepanovich; TSUKKER, G.Ye.,
red.; FREGER, D.P., red.izd-va

[Cold extrustion; a review] Kholodnoe vydavlivanie; obzor. Leningrad. (Leningradskii dom nauchno-tekhnicheskoi propagandy. Seriia: Goriachaia i kholodnaia obrabotka metallov davleniem) No.2. 1961. 47 p. (MIRA 15:6)

(Extrustion (Metals))

ZUYEV, A.B.; MASYUKEVICH, A.V.; SHILOV, V.V.

Equipment for automatic temperature regulation of die-casting molds. Mashinostroitel' no.10:6-7 O '65. (MIRA 18:10)

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

3RD AND 4TH ORDERS

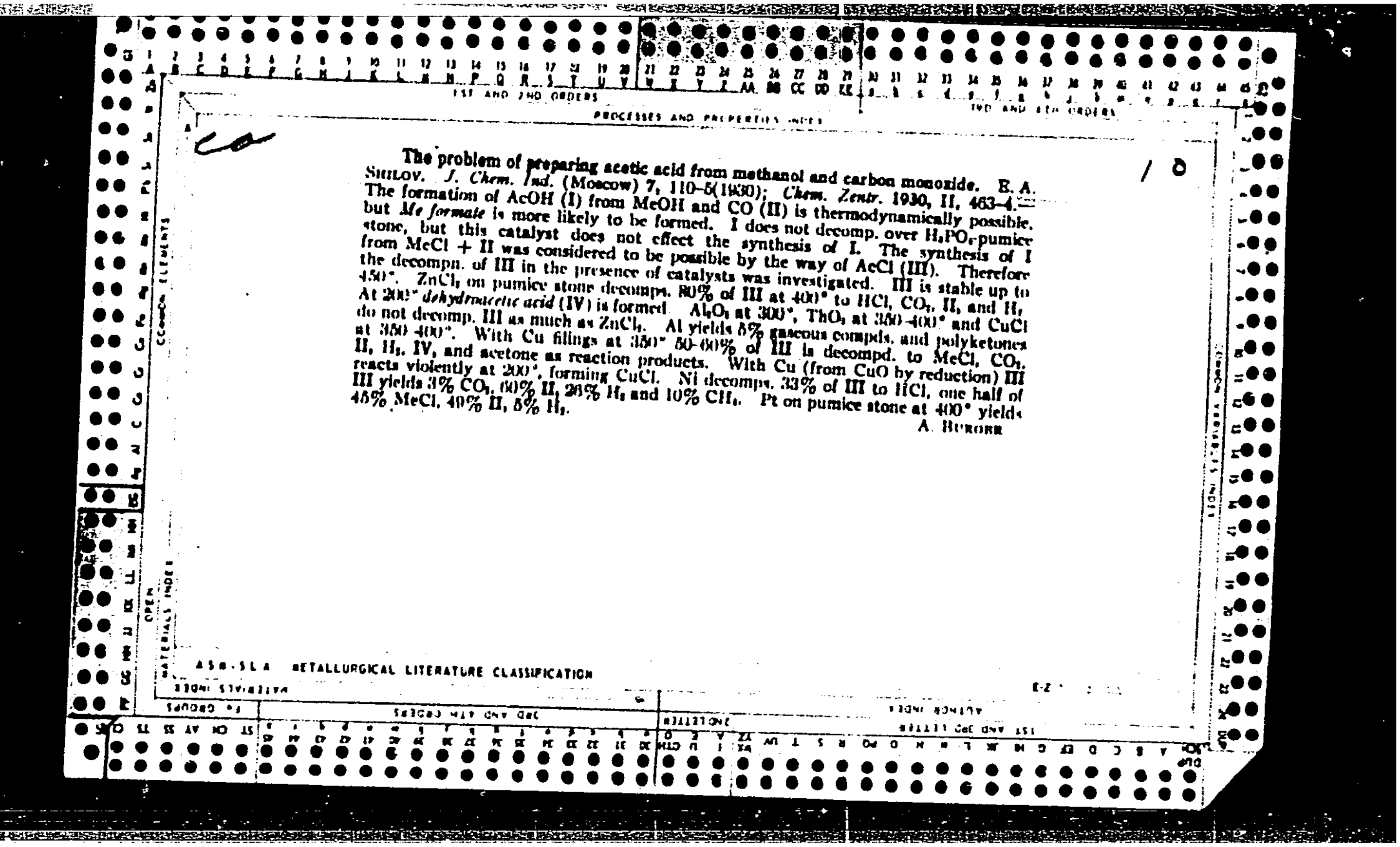
βC

Chlorination of acetic acid. E. A. Shilov (J. Chem. Ind., Russia, 1929, 6, 538—540).—The yield of monochloroacetic acid when a catalyst composed of iodine, phosphorus, and phosphorus pentachloride is used (cf. preceding abstract) is 75—90%. The use of phosphorus pentachloride is unnecessary. The reaction appears to be autocatalytic; on addition of monochloroacetic acid, especially in presence of a small quantity of sulphuric acid, chlorination takes place energetically in the absence of a metalloid catalyst.

CHEMICAL ABSTRACTS.

MATERIALS INDEX

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



Ca

1 0

The problem of preparing acetic acid from methanol and carbon monoxide. E. A. Shilov. *J. Chem. Ind.* (Moscow) 7, 110-5(1930); *Chem. Zentr.* 1930, II, 463-4.— The formation of AcOH (I) from MeOH and CO (II) is thermodynamically possible, but *Me formate* is more likely to be formed. I does not decomp. over H_3PO_4-pumice stone, but this catalyst does not effect the synthesis of I. The synthesis of I from MeCl + II was considered to be possible by the way of AcCl (III). Therefore the decompn. of III in the presence of catalysts was investigated. III is stable up to 450°. $ZnCl_2$ on pumice stone decomps. 80% of III at 400° to HCl, CO_2, II, and H_2. At 200° *dehydroacetic acid* (IV) is formed. Al_2O_3 at 300°, ThO_2 at 350-400° and CuCl do not decomp. III as much as $ZnCl_2$. Al yields 5% gaseous compds. and polyketones at 350-400°. With Cu filings at 350° 50-60% of III is decompd. to MeCl, CO_2, II, H_2, IV, and acetone as reaction products. With Cu (from CuO by reduction) III reacts violently at 200°, forming CuCl. Ni decomps. 33% of III to HCl, one half of III yields 3% CO_2, 60% II, 26% H_2 and 10% CH_4. Pt on pumice stone at 400° yields 45% MeCl, 40% II, 5% H_2.

A. Burokr

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

E-Z

PROCESSES AND PROPERTIES INDEX

10

Derivatives of triphenylethylene, and 1-phenyl-2,2-dibiphenylethylene. B. A. Smitov. *J. Russ. Phys.-Chem. Soc.* 62, 95-9(1930).—The synthesis and properties of triarylnitroethylenes and their derivs. are here investigated. When 25 g. of Ph_2C:CHPh (I) in dry PhH, petroleum ether, or 100% AcOH, are treated with N_2O_4 (from As_2O_3 and HNO_3, d. 1.4) there are obtained 35 g. of a crude product (II), sol. in Et_2O, PhH, $CHCl_3$, sparingly sol. in alc. and petroleum ether, which is presumed to be 1,2-dinitro-1,1,2-triphenylethane (III). The attempts to recryst. it from dil. alc. or AcOH at a moderate temp. produced 2-nitro-1,1,2-triphenyl-1-ethanol (IV), needles, m. 122-2.5°. Heating III and IV in AcOH gives triphenylnitroethylene (V), which is also obtained by shaking III in PhH with KOH (the yield in both cases is 30%), m. 175-6°, sparingly sol. in alc., Et_2O, more easily sol. in PhH, hot alc. and acetone, easily sol. in hot 100% AcOH. II heated in AcOH gives in addn. to V a good yield of Ph_2CO and p-$C_6H_4(NO_2)CO_2H$. For prepn. of 1-phenyl-2,2-dibiphenylylethylene, a mixt. of PhH and $(PhC_6H_4)_2CO$ (Adam, *Ann. Chim.* 15, 258(1888). Straus and Duetzmann, *C. A.* 16, 1239) was added to PhMgCl in Et_2O, the reaction mass worked up with acid, the ether layer sepd. and evapd., the residue treated with steam, filtered and recrystd. from 100% AcOH, m. 195-6°, needles, sol. in PhH and $CHCl_3$, sparingly sol. in 100% AcOH, insol. in alc. and Et_2O.
CHAS. BLANC

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PROCESSES AND PROPERTIES INDEX

cp

10

Preparation of vinylacetylene by the Willstätter and Wirth method. E. A. Shilov, A. N. Makashina, A. J. Smirnova and G. I. Yakimov. *Sinteticheskii Kauchuk* 1933, No. 1, 4-12.—The procedure for prepn. of vinylacetylene by the Willstätter and Wirth method is described. The following modifications of the method are suggested: (1) 1,4-Butylene dibromide can be easily obtained directly from tech. grade bivinyl (butadiene) by the Thiele method. (2) The use of NMe_3 instead of $NHMe_2$ in the reaction $BrCH_2CH:CHCH_2Br + 2NMe_3$ (in dry MeOH) = $BrMe_3NCH_2CH:CHCH_2NMe_3Br$ was found more satisfactory. The dibromide is next shaken with water and pptd. Ag_2O to form $HOMe_3NCH_2CH:CHCH_2NMe_3OH$ which is then distd., drop by drop, and the $CH_2:CHC:CH$ recovered in a liquid-air condenser. James Sorrel

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

E-2

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

30

Condensation of acetaldehyde to aldol. (Production of butadiene from 1,3-butylene glycol.) E. A. Shilov and G. I. Yakimov. *Sintet. Kauchuk* 1934, No. 4, 7-12.—Condensation was carried out by the addn. of NaOH (0.4 cc. of 10% NaOH per 20 g. of AcH as standard). The speed of reaction increases with the proportion of catalyst and with an increase in temp. The presence of ether retards the reaction. The reaction stops upon reaching a certain limit. Water and alcs. do not change the limit of condensation. A. Pestoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

CR

2

Kinetics of the addition of hypochlorous acid to a double bond. I. Hypochlorous acid and crotonic acid. E. A. hilov and N. P. Kanyaev. *J. Phys. Chem.* (U. S. S. R.) , 654-72(1934).—In the absence of other substances the addn. of HOCl to $\mathrm{MeCH{:}CHCO_2H}$ in aq. solns. from .003 to 0.05 *M* proceeds according to the trimol. equation $dx/dt = k[\mathrm{HOCl}]^2[\mathrm{C_4H_6O_2}]$. The presence of Cl acts catalytically and lowers the order of the reaction to the 2nd: $-d[\mathrm{HOCl}]/dt = k[K \times k][\mathrm{HOCl}][\mathrm{Cl^-}]$, where $[K \times k]$ is the total concn. of mol. and ionic crotonic acid. At 0°, $k = 38.3 \times 10^3$. The value of k increases with H-ion concn. and the complete kinetic equation is $-d[\mathrm{HOCl}]/dt = k[\mathrm{HOCl}][K][\mathrm{HCl}] + k_1[\mathrm{HOCl}][k][\mathrm{HCl}]$. The energy of activation is 7570 cal. from 0° to 20° and the action const. α is 4.8×10^{10}. *Pure HOCl soln.* was prepd. by treating Cl water with $\mathrm{Ag_3PO_4}$ till free from Cl odor, and then filtering. This soln. had a mol. cond. of 0.40 at diln. 120 at 0°.

F. H. Rathmann

COMMON ELEMENTS

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COMMON VARIABLES INDEX

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

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3RD AND 4TH ORDERS

Ch

The rate of hydrolysis of chlorine. E. A. Shilov and .. V. Kupinskaya. *Compt. rend. acad. sci. U. R. S. S.* 222-4(in English 224)(1936).—The rate of the reaction $Cl_2 + H_2O = HOCl + H^+ + Cl^-$ was measured by detg. the elec. cond. of Cl solns. The hydrolysis of Cl proceeds very rapidly even at 0°. When a concd. soln. of Cl was add., the cond. reached its final value in 2 min., but measurements made in the 1st min. give values somewhat below the final value. The rate is therefore rapid but finite.

R. R. Rushton

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

3RD AND 4TH ORDERS

PROCESSES AND PROPERTIES INDEX

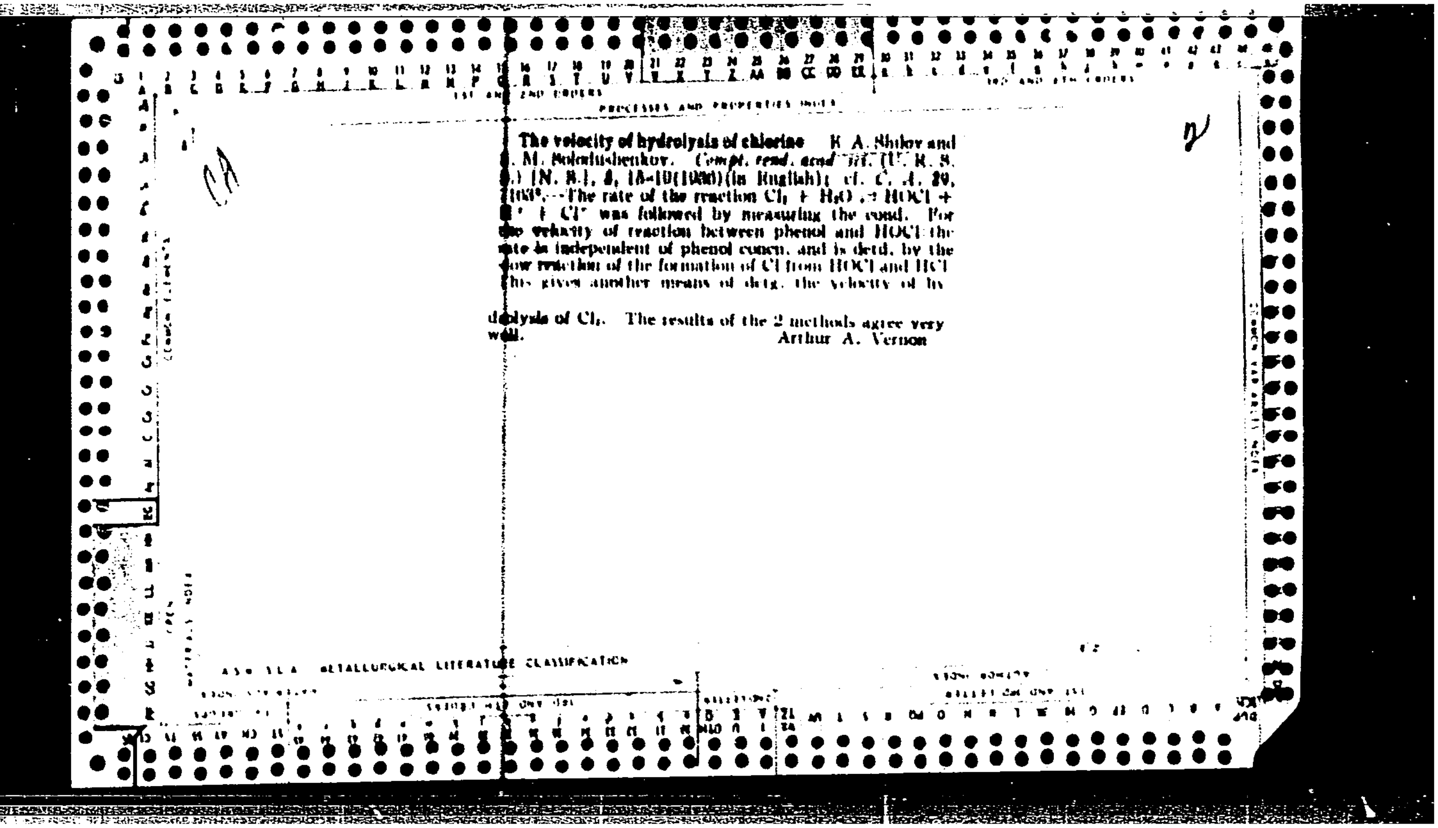
ca

10

The limit of the aldol condensation of acetaldehyde. U. A. Shilov. *J. Applied Chem.* (U. S. S. R.) 8, 93-8 (1935).—The condensation was carried out with 2.5% NaOH as catalyst. It is concluded that the condensation of AcH to aldol is caused not by conditions of an equil. but by the formation of a compd. of the aldol and the aldehyde which probably has the structure of a cyclic semiacetal MeCH.O.CHMe.CH$_2$.CH(OH).O. Twelve references.

A. A. Boehtlingk

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



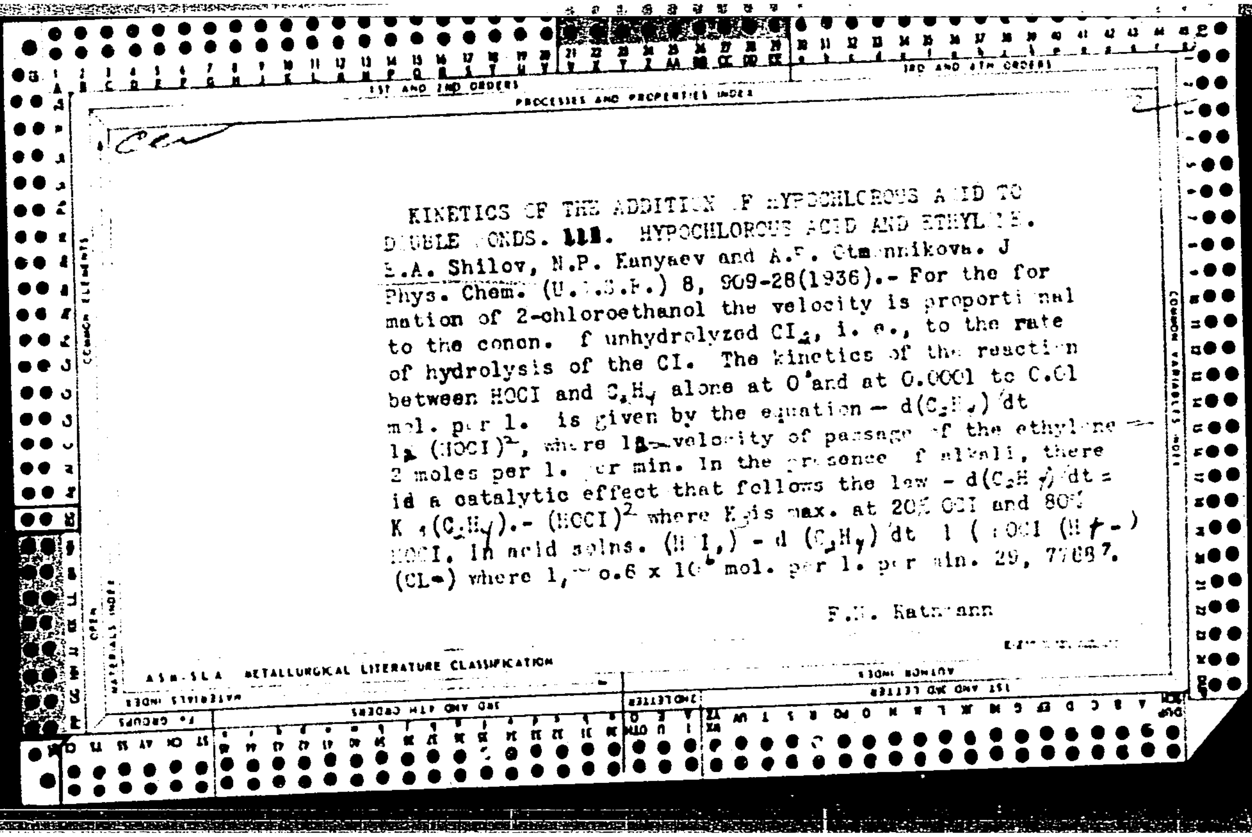
1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

The velocity of hydrolysis of chlorine E. A. Shilov and . M. Solodushenkov. *Compt. rend. acad. sci.* (U. R. S. .) [N. S.], 4, 15-19(1936)(in English); cf. C. A. 29, 1083.—The rate of the reaction $Cl_2 + H_2O \rightleftharpoons HOCl + ^+ + Cl^-$ was followed by measuring the cond. For the velocity of reaction between phenol and HOCl the rate is independent of phenol concn. and is detd. by the slow reaction of the formation of Cl from HOCl and HCl This gives another means of detg. the velocity of hydrolysis of Cl_2. The results of the 2 methods agree very well.

Arthur A. Vernon

A S M - S L A METALLURGICAL LITERATURE CLASSIFICATION



KINETICS OF THE ADDITION OF HYPOCHLOROUS ACID TO
DOUBLE BONDS. III. HYPOCHLOROUS ACID AND ETHYLENE.
E.A. Shilov, N.P. Kanyaev and A.F. Ctmannikova. J
Phys. Chem. (U.S.S.R.) 8, 909-28(1936).- For the for
mation of 2-chloroethanol the velocity is proportional
to the concn. of unhydrolyzed Cl_2, i. e., to the rate
of hydrolysis of the Cl. The kinetics of the reaction
between HOCl and C_2H_4 alone at 0° and at 0.0001 to 0.01
mol. per l. is given by the equation $- d(C_2H_4)/dt$
$l_1 (HOCl)^2$, where l_1 = velocity of passage of the ethylene
2 moles per l. per min. In the presence of alkali, there
id a catalytic effect that follows the law $- d(C_2H_4)/dt =$
$K_1(C_2H_4)$.- $(HOCl)^2$ where K_1 is max. at 20% OCl and 80%
HOCl. In acid solns. (HCl,) $- d(C_2H_4)/dt$ l (HOCl) (H^+-)
(Cl^-) where l_1 ~ 0.6 x 10^6 mol. per l. per min. 29, 7768^7.

F.H. Rathmann

1ST AND 2ND ORDERS

PROCESSES AND PROPERTIES INDEX

CA

this purpose are set forth comparatively.

New theories in the chemistry of chlorine bleaching. E. A. Shilov. *Khlopchatobumazhnaya Prom.* 1937, No. 1, 36-8; *Khim. Referat. Zhur.* 1, No. 3, 101 (1938).—The author proposes a new theory of Cl bleaching according to which this process is a destruction of the colored compds. The OH and NH_2 groups activate the entrance of Cl into the mol. of the aromatic compd. Other groups (NO_2, COOH, SO_3H, etc.) are deactivating. Both groups are contained in the mol. of different dyes. During the reaction first the chlorination of the dye takes place—then its disintegration into the *o*- and the *p*-forms. The addn. of increasing amts. of H_2SO_4 increases the speed of the reaction, while the addn. of a base first increases—later decreases it. The max. speed of reaction takes place in a basic soln. The cause of the decrease in the bleaching speed is the selective adsorption of the base and of HClO by the fiber, as a result of which a greater NaOH/HClO ratio is formed on the surface than in the soln. Intermediate complements are formed during the addn. of HClO to the aromatic ring which are stabilized into chlorohydrins in aliphatic compds. and as substitution products in aromatic compds. The catalytic action of acids and bases is the result of the formation of intermediate compds. more active than HClO. Only one practical conclusion is made—Cl bleaching must be done in an acid soln. W. R. Henn

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

1ST AND 2ND ORDERS

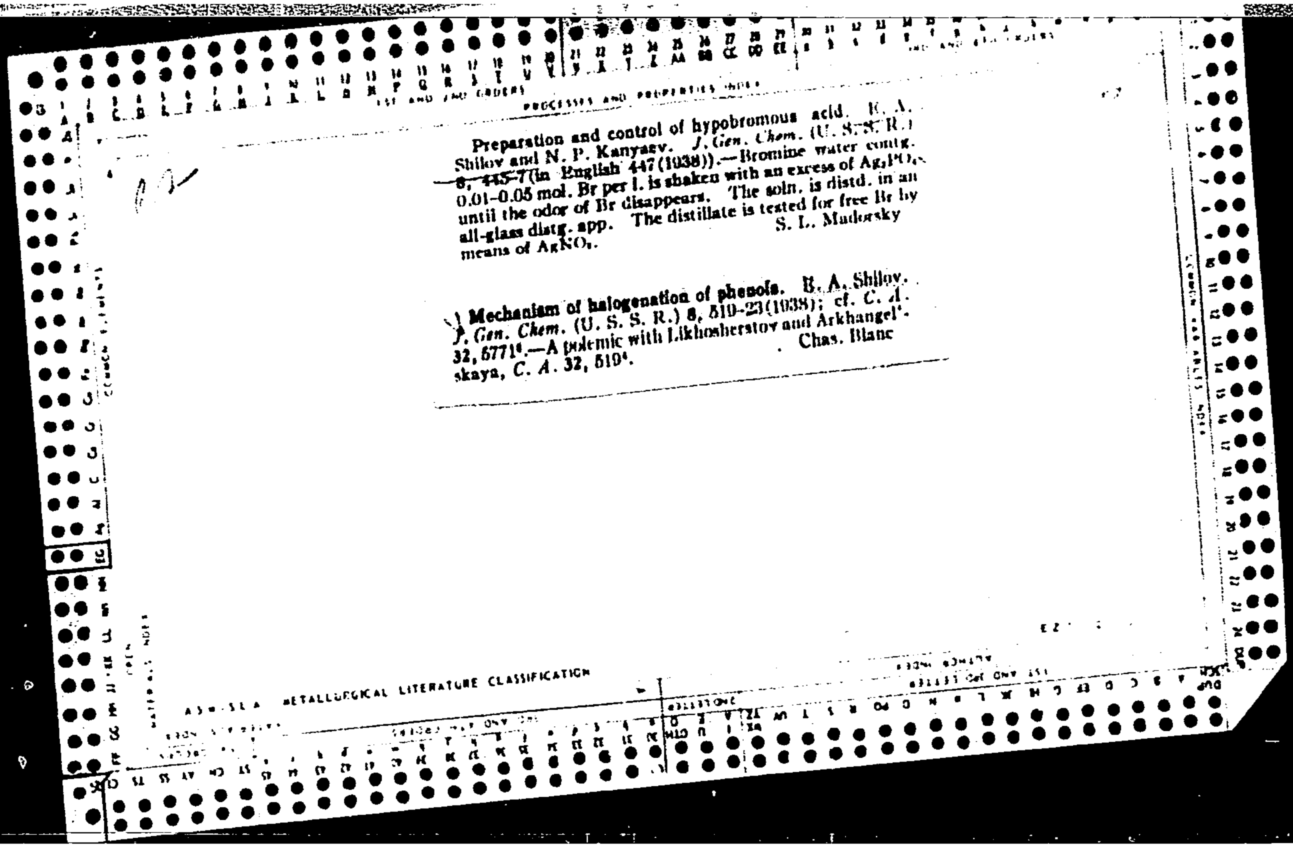
PROCESSES AND PROPERTIES INDEX

CA

2

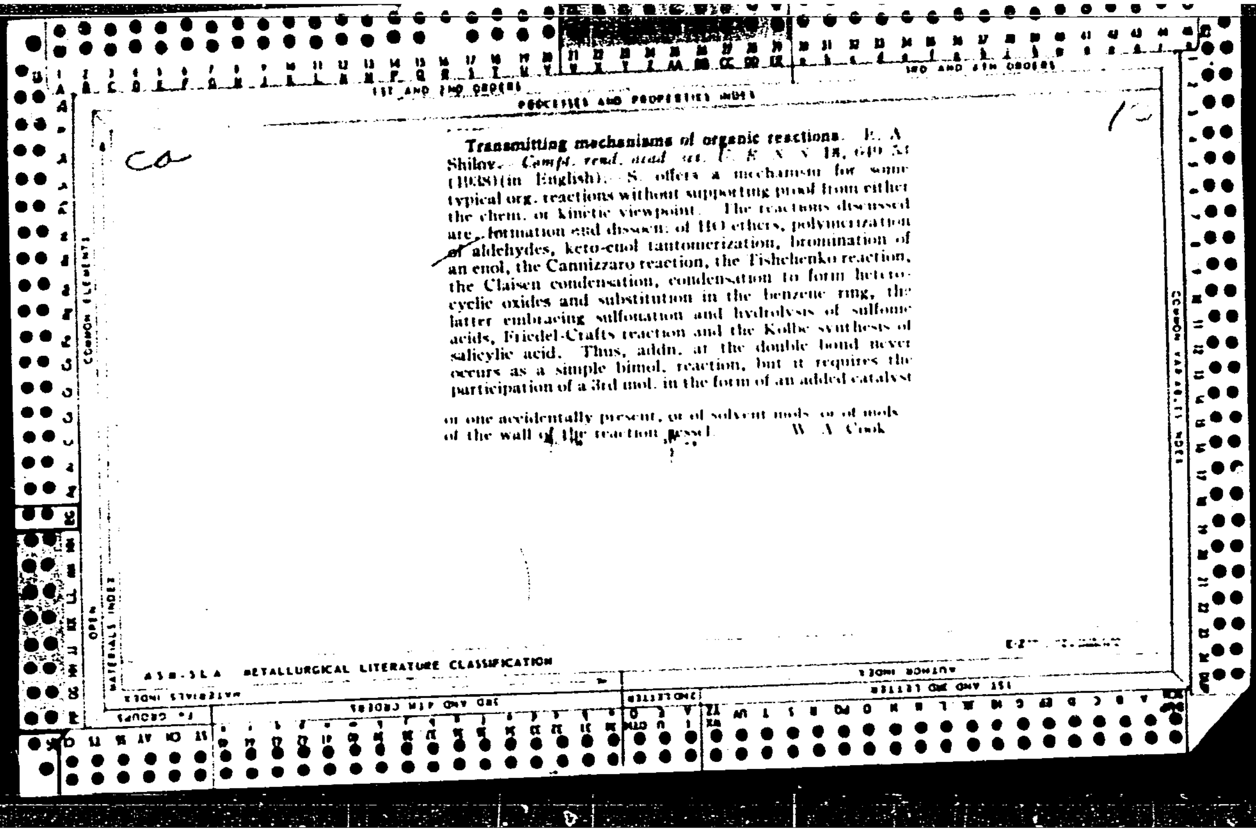
Kinetics of the addition of hypochlorous acid at double bonds. IV. Hypochlorous acid and 2-butene-1,4-diol. E. A. Shilov and N. P. Kanyaev. *J. Phys. Chem.* (U. S. S. R.) 10, 123-31(1937); cf. *C. A.* 31, 2075^{3}.—The kinetics of the reaction $HOCl + HOCH_2—CH{=}CH—CH_2OH \rightarrow HOCH_2—CHOH—CHCl—CH_2OH$ in aq. soln. at 0° obeys the 3rd-order equation $d[C{=}C]/dt = k_3[HOCl]^2[C{=}C]$ where $k_3 = 950$ moles/l. min. at low concns. while at higher concns. the exponents 2 and 1 are replaced by 1.9 and 0.7, resp. HCl acts as a pos. catalyst and the order of reaction is given by the equation $d[C{=}C]/dt = k_1[HOCl][H^+][Cl^-]$ where $k_1 = 4 \times 10^3$ or nearly the value for the coeff. of rehydrolysis of Cl_2, indicating that Cl_2 mols. play a deciding role in the mechanism of the reaction. In alk. soln. the kinetics is expressed by $d[C{=}C]/dt = q[HOCl][OCl^-][C{=}C]$ where $q = 92,000$ up to 15 mole % NaOH, and decreases at higher concns. of either NaOH or of HOCl. The complete reaction consists of consecutive stages of which the butene-2-diol-1,4 ion is one. F. H. Rathmann

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



Preparation and control of hypobromous acid. B. A. Shilov and N. P. Kanyaev. *J. Gen. Chem.* (U. S. S. R.) 8, 445-7(in English 447(1938)).—Bromine water contg. 0.01-0.05 mol. Br per l. is shaken with an excess of Ag_3PO_4 until the odor of Br disappears. The soln. is distd. in an all-glass distg. app. The distillate is tested for free Br by means of $AgNO_3$. S. L. Madorsky

Mechanism of halogenation of phenols. B. A. Shilov. *J. Gen. Chem.* (U. S. S. R.) 8, 519-23(1938); cf. *C. A.* 32, 6771^9.—A polemic with Likhosherstov and Arkhangel'skaya, *C. A.* 32, 519^4. Chas. Blanc



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Transmitting mechanisms of organic reactions. E. A. Shilov. *Compt. rend. acad. sci. U. R. S. S.* 18, 649-52 (1938)(in English). S. offers a mechanism for some typical org. reactions without supporting proof from either the chem. or kinetic viewpoint. The reactions discussed are formation and dissocn. of HCl ethers, polymerization of aldehydes, keto-enol tautomerization, bromination of an enol, the Cannizzaro reaction, the Tishchenko reaction, the Claisen condensation, condensation to form heterocyclic oxides and substitution in the benzene ring, the latter embracing sulfonation and hydrolysis of sulfonic acids, Friedel-Crafts reaction and the Kolbe synthesis of salicylic acid. Thus, addn. at the double bond never occurs as a simple bimol. reaction, but it requires the participation of a 3rd mol. in the form of an added catalyst or one accidentally present, or of solvent mols. or of mols. of the wall of the reaction vessel. W. A. Cook

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1A

Di- and polyarylethanes. I. Di-p-xenylethanone and its derivatives. E. A. Shilov and F. K. Yudin. *J. Gen. Chem.* (U. S. S. R.) 10, 167-72(1940). The stem "xen" of xenyl, proposed by Hale (*C. A.* 27, 76) as a basis for the nomenclature of Ph_2 and its derivs., is used in this series. *p-Xenoin*, $PhC_6H_4CH(OH)COC_6H_4Ph$ (I), was prepd. from p-PhC_6H_4CHO (cf. Hey, *C. A.* 26, 442) by condensation with KCN in dil. alc. by the method of Gomberg and Van Natta (*C. A.* 23, 3022). The addn. of 20 g. Zn dust in the course of 2-3 hrs. into boiling 20 g. I in 1 l. of 100% AcOH and the recrystn. of the ppt. from boiling xylene yielded 34% *di-p-xenylethanone*, $PhC_6H_4CH_2COC_6H_4Ph$, (II), m. 229-30°. It is practically insol. in cold and sparingly sol. in hot org. solvents with a strong dark blue fluorescence. Its *oxime* m. 173.5-4°. II is but little enolized. It does not react with $FeCl_3$, Ac_2O and AcCl. With 1 and 2 mols. Br in $CHCl_3$ and heating, II gave $PhC_6H_4CHBrCOC_6H_4Ph$, m. 186-7.5° (C_6H_6), and the *dibromide*, m. 181-3°, resp. The attempts to obtain Br derivs. of II from I with HBr at 130-40° and with PBr_3 in Et_2O on refluxing produced *di-p-xenylethanedione*, m. 142°. Engler and Grumm (*Ber.* 30, 2923(1897)) observed analogous dismutation of benzoin and its derivs. I and PBr_3 formed II. A suspension of 10 g. I in 100 ml. of hot $CHCl_3$ reacts with $SOCl_2$ to give 43% $PhC_6H_4CHClCOC_6H_4Ph$, m. 164.5-6°. II reacts with aryl magnesium bromides to give *triarylethanols*, which with HCl in C_6H_6 are decompd. to form the corresponding *ethene derivs*. *1-Phenyl-1,2-di-p-xenylethanol*, $Ph(PhC_6H_4)C(OH)CH_2C_6H_4Ph$, m. 218.5° (from PhMgBr and II), gives a crimson soln. in concd. H_2SO_4. With HCl or 100% AcOH it gave $PhC_6H_4CH{:}C(C_6H_4Ph)Ph$, m. 198.5-200° ($C_6H_6$). This in CS_2 with Br yielded an α-bromide, m. 212-33°, probably a mixt. of cis and trans isomers. *1-(α-Naphthyl)-1,2-di-p-xenylethanol*, m. 188° (from α-$C_{10}H_7MgBr$ and II), gives an intensely green soln. in H_2SO_4, changing on standing or heating to crimson. The *ethene deriv.*, m. 209-14°. **II. Synthesis of 1,2,3,4-tetra-p-xenylbutane-1,4-dione and tetra-p-xenylfuran.** F. K. Yudin. *Ibid.* 173-5.—$(PhC_6H_4CHCOC_6H_4Ph)_2$ (III), m. 297-300.5°, was obtained (1) from II in C_5H_5N by oxidizing with excess of $Cu(NO_3)_2$ on a water bath (cf. Gomberg and Van Natta, *loc. cit.*), pouring into H_2O and recrystg. the ppt. from xylene; (2) from the ms-Br and ms-Cl derivs. of II by condensation with Naturkupfer C in PhMe. Unlike II but like bianthrone, III solns. do not fluoresce, indicating the absence of enolization, but on the addn. of H_2SO_4 give a strong blue fluorescence. III with excess AcCl in a sealed tube on heating at 110° for 4 hrs. or at 180-200° for 2 hrs. gave 100% of *tetra-p-xenylfuran*, m. 281-2.5°, sparingly sol. in org. solvents with intense fluorescence. Chas. Blanc

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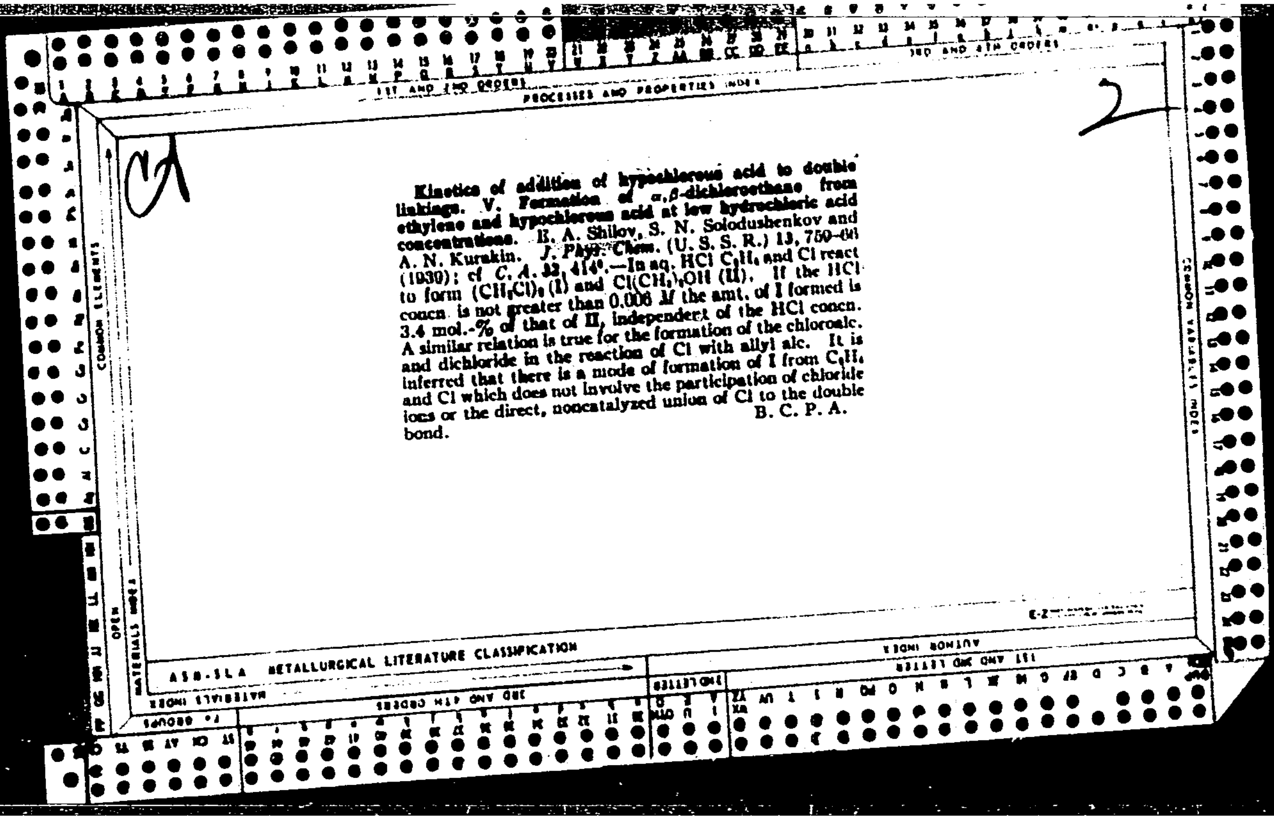
Lab. Org. Chem., Ivanovo Chem.-Tech. Inst.

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



Cl

2

Kinetics of addition of hypochlorous acid to double linkings. V. Formation of α,β-dichloroethane from ethylene and hypochlorous acid at low hydrochloric acid concentrations. E. A. Shilov, S. N. Solodushenkov and A. N. Kurakin. *J. Phys. Chem.* (U. S. S. R.) 13, 750-66 (1939); cf. *C. A.* 33, 414^6.—In aq. HCl C_2H_4 and Cl react to form $(CH_2Cl)_2$ (I) and $Cl(CH_2)_2OH$ (II). If the HCl concn. is not greater than 0.008 *M* the amt. of I formed is 3.4 mol.-% of that of II, independent of the HCl concn. A similar relation is true for the formation of the chloroalc. and dichloride in the reaction of Cl with allyl alc. It is inferred that there is a mode of formation of I from C_2H_4 and Cl which does not involve the participation of chloride ions or the direct, noncatalyzed union of Cl to the double bond.

B. C. P. A.

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Bromine cation as a brominating agent. Evgenii Shilov and Nikolai Kanyaev. *Compt. rend. acad. sci. U. R. S. S.* 24, 890-2(1939)(in English).—Since the velocity of the reaction between Na *m*-anisole sulfonate and HOBr varies directly with the concn. of both HOBr and H^+ ion in the soln., the Br cation is probably the actual brominating agent. When the bromination was carried out in the presence of HBr or HCl (instead of HNO_3 or H_2SO_4), the Br and BrCl formed acted as independent brominating agents, their activities being detd. by their tendencies to polarize into Br^+X^-. The velocity of bromination of Na *m*-anisolesulfonate increases in the following order for the various brominating agents: BrOH, Br, BrCl, Br ion.

George Ayers

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The kinetics of bromination of sodium m-anisolesulfonate in aqueous solution. N. P. Knyazev and E. A. Shilov.—Trans. Inst. Chem. Tech. Ivanovo (U. S. S. R.) 1940, No. 3, 53-60.—See C. A. 35, 371¹. W. R. H.

Constants of some equilibrium reactions of hypobromous acid. N. P. Knyazev and E. A. Shilov.—Trans. Inst. Chem. Tech. Ivanovo (U. S. S. R.) 1940, No. 3, 60-73.—The sp. elec. cond. of HCl solns. contg. HOBr was measured. Into a flask (with a ground stopper) in an ice thermostat was introduced 20 ml. of a titrated soln. of HCl and HOBr which had been cooled to 0°. The soln. was mixed, transferred to a vessel with platinized electrodes in an ice thermostat and the elec. cond. measured at 0°. Parallel expts. were made under identical conditions with water instead of HOBr. From the decrease of the elec. cond. the hydrolysis const. of BrCl was found to be equal to 2.94×10^{-4}. The concn. of Br cation in mixts. of HOBr and HNO_3 solns. is so small that it cannot be detd. by the elec.-cond. method. The compn. of equil. mixts. of HOBr and Br^- can be calcd. by means of the consts. of some chem. equilibria. Nine references. W. R. Henn

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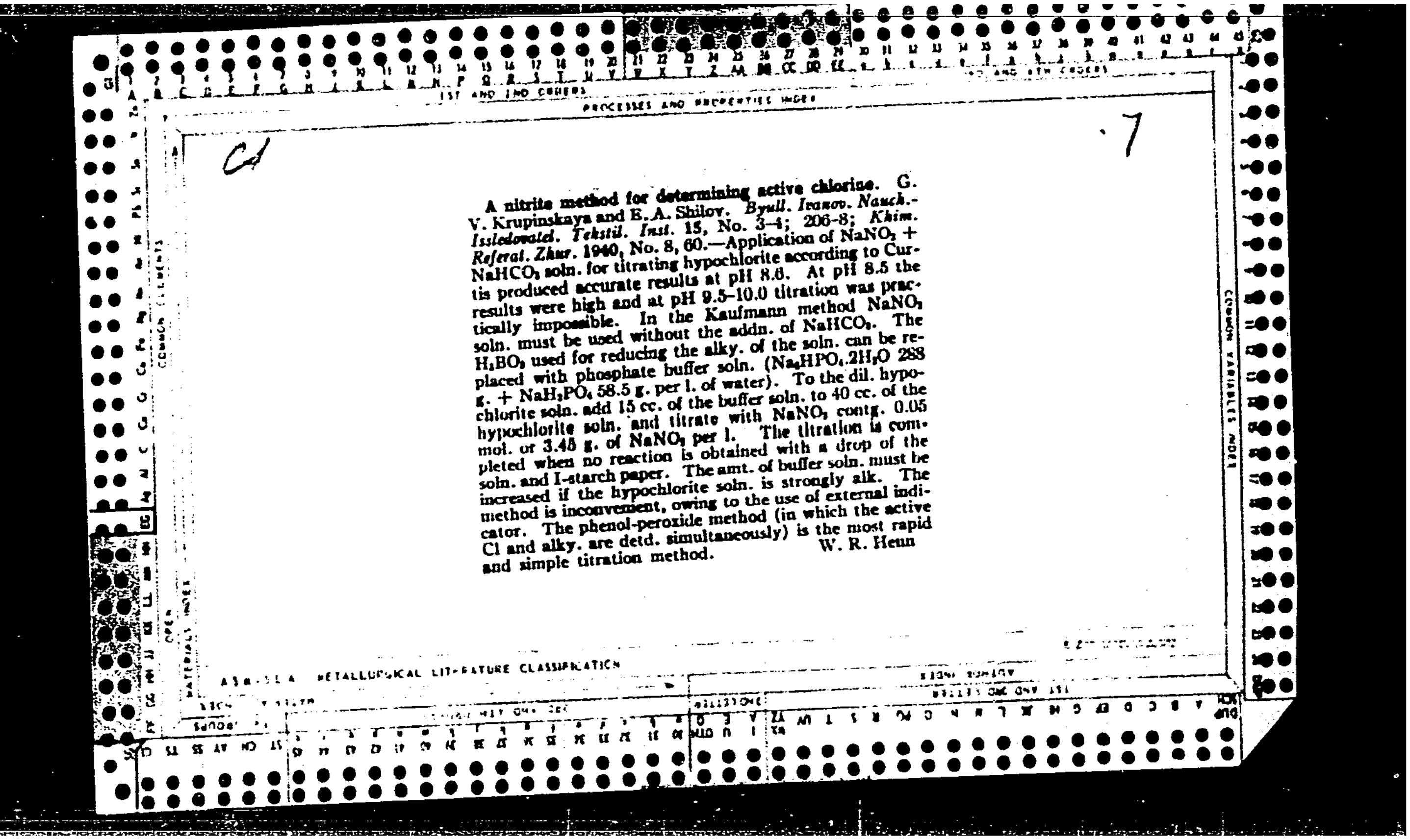

A nitrite method for determining active chlorine. G.
V. Krupinskaya and E. A. Shilov. *Byull. Ivanov. Nauch.-*
Issledovatel. Tekstil. Inst. 15, No. 3-4; 206-8; *Khim.*
Referat. Zhur. 1940, No. 8, 60.—Application of $NaNO_2$ +
$NaHCO_3$ soln. for titrating hypochlorite according to Cur-
tis produced accurate results at pH 8.8. At pH 8.5 the
results were high and at pH 9.5–10.0 titration was prac-
tically impossible. In the Kaufmann method $NaNO_2$
soln. must be used without the addn. of $NaHCO_3$. The
H_3BO_3 used for reducing the alky. of the soln. can be re-
placed with phosphate buffer soln. ($Na_2HPO_4.2H_2O$ 288
g. + NaH_2PO_4 58.5 g. per l. of water). To the dil. hypo-
chlorite soln. add 15 cc. of the buffer soln. to 40 cc. of the
hypochlorite soln. and titrate with $NaNO_2$ contg. 0.05
mol. or 3.45 g. of $NaNO_2$ per l. The titration is com-
pleted when no reaction is obtained with a drop of the
soln. and I-starch paper. The amt. of buffer soln. must be
increased if the hypochlorite soln. is strongly alk. The
method is inconvenient, owing to the use of external indi-
cator. The phenol-peroxide method (in which the active
Cl and alky. are detd. simultaneously) is the most rapid
and simple titration method. W. R. Henn

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Intramolecular migrations of hydrogen and of radicals during organic transformations. E. A. Shilov. *Doklady Akad. Nauk S. S. S. R.* 30, 210-22(1941).—S. proposes a new type of migration mechanism for reactions involving mol. rearrangements. The H atom or the radical involved in the rearrangement, according to this theory, forms an intermediate complex in the form of a 3-membered ring with the 2 adjacent C atoms which are involved in the rearrangement. Both electrophilic and nucleophilic agents can initiate the reaction. A no. of rearrangements are cited as supporting the theory. The contention that the migrating group at no time becomes sepd. from the mol. is supported by: lack of such by-products which would indicate the formation of free radicals or ions and the preservation by the migrating group of its optical configuration during rearrangement. The tracing of these reactions by tracer atoms (D) is suggested as a means of proof of the theory.

G. M. Kosolapoff

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6

Reaction of hypochlorites with nitrites. E. A. Shilov. *J. Applied Chem.* (U.S.S.R.) 17, 354-5(1944).—At pH 5-8, concns. of HOCl in hypochlorite soln. of a given concn. do not change appreciably in the presence of nitrites, because in all cases considerable hydrolysis occurs; this is true over 1000-fold variation of HNO_2 concn. At increased pH values the concns. of HNO_2 and HOCl decrease to a similar extent and at pH 10 oxidation of the nitrite is essentially stopped. G. M. Kosolapoff

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A pneumatic regulator for titration. E. A. Shilov. *Zavodskaya Lab.* 11, No. 1, 102-3(1945); cf. *C.A.* 23, 1531.—Construction details are given for a regulator in which the membrane consists of a flat rubber bulb, operated by a screw. The diam. of the membrane is detd. by the vol. of the liquid to be drawn; a 9-cm. membrane draws approx. 25 ml. of the liquid. Six references.

W. R. Henn

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Catalytic ignition of mixtures of chlorine with ethylene and other combustible gases. K. A. Shilov (Ivanovsk. Chem.-Technol. Inst.; Org. Chem. Lab.). *J. Gen. Chem.* (U.S.S.R.) 15, 135-41(1945)(English summary); cf. *C.A.* 39, 4791^{1}.—Admixts. of oxides of Hg, Ag, and Pb lower the ignition temp. of Cl-ethylene mixts., so that explosions occur even at room temp. Mixts. of Cl with H_2 or CH_4 explode at room temp. over yellow Hg oxide. The catalytic effect is connected with heats of formation of the oxides and chlorides.

G. M. Kosolapoff

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The synthesis of 2-chloroethanol. I. The pseudocatalytic action of copper salts in the preparation of 2-chloroethanol by the method of Gomberg. E. A. Shilov, N. P. Kanyaev, and S. N. Solodushenkov (Ivanov Chem.-Tech. Inst.). *J. Gen. Chem.* (U.S.S.R.) 15, 701-5(1945).—Careful repetition of the methods described in the literature show that any apparent catalytic effect of Cu salts on the combination of C_2H_4 and Cl in H_2O was due to exptl. error.

H. M. Leicester

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Some data on the preparation of acetylsulfanilyl chloride. E. A. Shilov and A. I. Kolenin. *J. Applied Chem.* (U.S.S.R.) 18, 113-20(1945).—It was shown that during the hydrolysis of acetylsulfanilyl chloride (I) there are formed at first acetylsulfanilic acid and HCl, followed in turn by AcOH and sulfanilic acid; as a by-product there is formed about 2% (acetylsulfanilyl)sulfanilic acid. Hydrolysis of Ac group is hastened by increase of H ion concn., hence by reduction of the vol. of water used. In a homogeneous water-Me_2CO soln. the hydrolysis of the SO_2Cl group occurs according to a 1st-order reaction, with the time of "half-hydrolysis" being 87 min. at 20°, 40 min. at 30°, and 18 min. at 40°. H ion does not affect the rate, but OH ion greatly accelerates it. The soly. of I in $(CH_2Cl)_2$, benzene, and their 1:1 mixt. was detd. at temps. between 0° and the b.p. The product may be recrystd. equally well from either dry state or from a moist paste when $(CH_2Cl)_2$ is used for solvent at 60-70°, with 15-20% retention in the mother liquor, which may be re-used 2-3 times.

G. M. Kosolapoff

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Continuous method for preparation of chloroacetone. E. A. Shilov and G. V. Kupinskaya. *J. Applied Chem.* (U.S.S.R.) 18, 121-6(1945).—An app. is described for the lab. continuous chlorination of Me_2CO, in which the reagents mix in a water-jacketed temp.-controlled column with the HCl removal being effected by washing with concd. $CaCl_2$ soln. When chlorination is carried only to 60-70%, the product is 99.0% pure *monochloroacetone*. The product, after washing, is fractionated. $CaCl_2$ soln. is regenerated by marble. Yields range from 1.1 to 1.25 kg. product per 1 kg. acetone. G. M. Kosolapoff

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Preparation of thiourea from calcium cyanamide. E. A. Shilov. *J. Applied Chem.* (U.S.S.R.) 18, 230 5(1945) (English summary).—Thiourea was prepd. from Ca cyanamide as follows: an almost satd. soln. of thiourea, contg. some yellow NH_4 sulfide, NH_4OH, and Ca hydrosulfide (this soln. is the mother liquor from previous runs) is treated with stirring with H_2S and Ca cyanamide (about 1 kg. of 40% $CaCN_2$ per 2 l. soln.). When H_2S satn. is complete at 25°, which takes about 1 hr., the mixt. is heated to 90°, with careful temp. control; the resulting reaction requires 10-15 min. for completion. The hot suspension is filtered, the product is washed with mother liquor and, finally, with distd. water. Cooling of the filtrate gives 300-380 g. thiourea per kg. Ca cyanamide. As a control analytical method that of Cuthill and Atkins (*C.A.* 31, 3417[7]) was used with the modification that the filtration of the Ag_2S ppt. was omitted; the decompn. of thiourea proceeds quantitatively in NH_4OH soln.

C. M. Kosolapoff

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Catalytic inflammation of chlorine-ethylene mixtures. E. A. Shilov. *Doklady Akad. Nauk S.S.S.R.* 46, 69-70; *Compt. rend. acad. sci. U.R.S.S.* 46, 61-5(1945)(in English). In glass tubes, the ignition temp. of mixts. of 75-33% Cl_2 with 25-67% C_2H_4 is within the limits 225-260°, depending somewhat on the compn. of the mixt. Certain oxides exert a powerful catalytic effect. Thus, ignition occurs at room temp. with HgO, Hg_2O, and Ag_2O and at 100-120°, or occasionally at 45°, with PbO. (However, Pb_3O_4 and PbO_2 are much less active.) The catalytic effectiveness of the metal oxides mentioned above is probably due to the Cl_2 interacting with the oxides to produce complex metal compds. contg. highly reactive, combined O capable of initiating reaction chains. Introduction of Cl_2O into Cl_2-C_2H_4 mixts. was not effective in reducing inflammation temp. Many metals and metal oxides, viz., Sb, Fe, CuO, Cu_2O, MgO, CdO, SnO_2, MoO_3, and Fe_2O_3, are catalytically inactive. J. W. Perry

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Formation of 2,2'-dichlorodiethyl ether in the synthesis of 2-chloroethanol. E. A. Shilov (Chem.-Tech. Inst., Ivanovo). *Compt. rend. acad. sci. U.R.S.S.* 47, 472-4; *Doklady Akad. Nauk S.S.S.R.* 47, 490-2(1945).—Assuming that $(CH_2ClCH_2)_2O$ (I) forms by reaction between C_2H_4, Cl_2, H_2O, and CH_2ClCH_2OH, 2 rate equations may be set up: (A) $dx/dt = k'[CH_2ClCH_2OH][C_2H_4][Cl_2]$, in which x is the concn. of I; and (B) $d[CH_2ClCH_2OH]/dt = k[C_2H_4][Cl_2] - k'[CH_2ClCH_2OH][C_2H_4][Cl_2]$. By combining A and B into a single expression, k'/k may be evaluated from the final concn. of I and the initial and final concns. of CH_2ClCH_2OH; expts. give k'/k as 0.021, const. over wide variations in the concn. of CH_2ClCH_2OH. C_2H_4 and Cl_2 were passed simultaneously at 20 ml./min. into a vertical tube 1 m. by 18 mm., contg. 300 ml. of H_2O solns. of CH_2ClCH_2OH of known concn. until satn. was reached; 6-12 hrs. was required. I was detd. by difference by distn. from 50-100 ml. of soln. in a Dina-Stark app., redistg. from 100 ml. H_2O (to remove CH_2ClCH_2OH), and removing I by concd. H_2SO_4 from the mixt. contg. I and $(CH_2Cl)_2$.

Orville J. Sweeting

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Series of aromatic ketenes: phenyl-4-biphenylylketene and α-phenyl-α-(1-naphthyl)ketene. S. I. Burmistrov and E. A. Shilov (Ivanovsk Chem. Tech. Inst.). *J. Gen. Chem.* (U.S.S.R.) 16, 295-9(1946).—Me 4-biphenylylglyoxylate ($b_{0.1}$ 207-9°, m. 61-2°) reacted with PhMgBr to yield *phenyl-4-biphenylylglycolic acid*, m. 164-7°, which on treatment with PCl_5 gave $Ph(PhC_6H_4)CClCOCl$ (I), m. 76° (from petr. ether). I (2 g.) was shaken with Hg in Et_2O under CO_2 in a sealed tube to yield *phenyl-4-biphenylylketene* (II), m. 102-4°, as yellow plates; treatment of II with $PhNH_2$ gave *α-phenyl-α-(4-biphenylyl)acetanilide*, m. 174°, while the use of dry NH_3 gave *α-phenyl-α-(4-biphenylyl)acetamide* (III), m. 230°. For identification, III was also prepd. by the hydrolysis in $AcOH-H_2SO_4$ of *phenyl-4-biphenylylacetonitrile*, m. 132-3° (from EtOH), which was prepd. by reaction of PhCH(OH)CN with PhH in the presence of $SnCl_4$. $BzCO_2Et$ (100 g.) and $1-C_{10}H_7MgBr$ (from 134 g. $C_{10}H_7Br$) gave 78 g. *phenyl-1-naphthylglycolic acid* (IV), m. 145-6° (from benzene) (*picrate*, m. 147-50° (from benzene)); treatment of IV with PCl_5 gave *phenyl-1-naphthylchloroacetyl chloride*, m. 154-5° (from benzene-petr. ether), which on prolonged shaking with Hg in Et_2O under CO_2 gave *phenyl-1-naphthylketene* (V), m. 90-1.5°, yellow prisms. The latter gave with NH_3 the *α-phenyl-α-(1-naphthyl)acetamide*, m. 120° (from benzene), which readily forms a *sesquihydrate*, m. 105-6° (from dil. EtOH). V and $PhNH_2$ yielded *α-phenyl-α-(1-naphthyl)acetanilide*, m. 227° (from 80% AcOH). II and V readily gave the corresponding diarylacetic acids on treatment with water.

G. M. Kosolapoff

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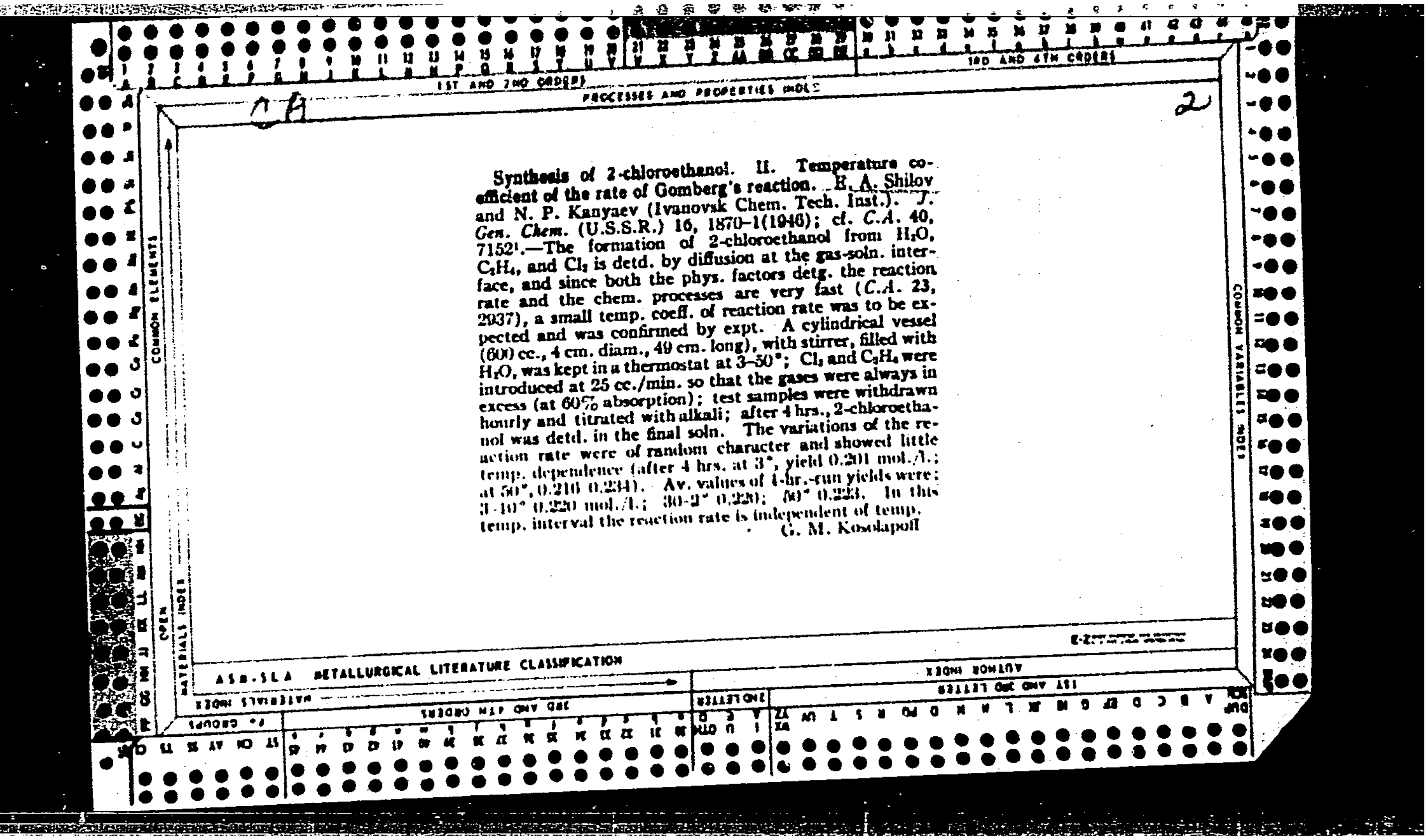

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Synthesis of 2-chloroethanol. II. Temperature coefficient of the rate of Gomberg's reaction. E. A. Shilov and N. P. Kanyaev (Ivanovsk Chem. Tech. Inst.). *J. Gen. Chem.* (U.S.S.R.) 16, 1870-1(1946); cf. *C.A.* 40, 7152¹.—The formation of 2-chloroethanol from H_2O, C_2H_4, and Cl_2 is detd. by diffusion at the gas-soln. interface, and since both the phys. factors detg. the reaction rate and the chem. processes are very fast (*C.A.* 23, 2937), a small temp. coeff. of reaction rate was to be expected and was confirmed by expt. A cylindrical vessel (600 cc., 4 cm. diam., 49 cm. long), with stirrer, filled with H_2O, was kept in a thermostat at 3-50°; Cl_2 and C_2H_4 were introduced at 25 cc./min. so that the gases were always in excess (at 60% absorption); test samples were withdrawn hourly and titrated with alkali; after 4 hrs., 2-chloroethanol was detd. in the final soln. The variations of the reaction rate were of random character and showed little temp. dependence (after 4 hrs. at 3°, yield 0.201 mol./l.; at 50°, 0.210 (0.234). Av. values of 4-hr.-run yields were: 3-10° 0.220 mol./l.; 30-2° 0.220; 50° 0.223. In this temp. interval the reaction rate is independent of temp.

G. M. Kosolapoff

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Gomberg's synthesis of 2-chloroethanol. III. Results of the presence and composition of the gaseous phase. E. A. Shilov and N. P. Kanyaev (Ivanovsky Chem.-Tech. Inst.). *J. Gen. Chem.* (U.S.S.R.) 17, 100-16 (1947)(in Russian); *cf. C.A.* 41, 6119*e*.—A gaseous mixt. of C_2H_4 and Cl in contact with an aq. soln. of the gases, vigorously agitated, forms $ClCH_2CH_2OH$ (I) and $(CH_2Cl)_2$ (II) in the same ratio as when the reaction takes place in a homogeneous soln. The amts. of each formed depend on the concn. of chloride ion in soln. The formation of II is a surface reaction and occurs only above the soln. on solid surfaces or liquid films. C_2H_4 and Cl_2 combine very slowly on an ice surface in the absence of a liquid phase. The ratio of I and II formed is independent of the C_2H_4-Cl_2 ratio. The rate of C_2H_4 absorption increases with increasing Cl concn. in the soln. but is less than proportional to it.

Arild J. Miller

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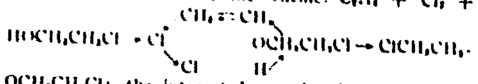
Synthesis of 2-chloroethanol. IV. Theory of formation of bis(2-chloroethyl) ether. Method of analysis of the reaction mixture. K. A. Shilov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 17, 1490–1502(1947)(in Russian); cf. *C.A.* 42, 4127*h*; 35, 371^4.—The formation of the $(ClCH_2CH_2)_2O$ in the Gomberg synthesis of $ClCH_2CH_2OH$ may be given by the scheme: C_2H_4 + Cl_2 +



$$\begin{array}{lcl} & \mathrm{CH_2{=}CH_2} & \\ \mathrm{HOCH_2CH_2Cl} + \mathrm{Cl} & & \mathrm{OCH_2CH_2Cl} \rightarrow \mathrm{ClCH_2CH_2\text{-}} \\ \quad\quad\quad\quad \mathrm{Cl} & & \mathrm{H} \end{array}$$

OCH_2CH_2Cl; the integrated equation for the reaction rate is $X = E_0 - E\frac{k}{k'}\ln\frac{k/k' - E_0}{k/k' - E}$, where *E* is the concn. of $ClCH_2CH_2OH$, E_0 is its initial concn., *X* is the concn. of the di-Cl ether, *k* is the reaction rate const. (see previous reference), calcd. without accounting for ether formation, and *k'* is the reaction rate const. for the formation of the di-Cl ether. Since *E* is small in comparison with *k/k'*, the approx. form is: $k'/k = 2X/(E^2 - E_0^2)$. A vertical tube 1 m. long and 18 mm. in diam. was provided with a stopcock at the bottom, near which the two inlets were sealed in; below the entrance of these was attached an ascending tube which terminated near the top of the reactor (this served as a circulating tube for the mixt.). The app. was kept in the dark and the reactions were conducted at 15–20°. The tube was charged with 300 ml. of soln., and Cl and C_2H_4 fed at 20 ml./min. over 5–12 hrs., with 60–70% absorption taking place. At the end of a run the Cl flow was stopped before the C_2H_4, in order to flush out any excess Cl. The mixt. was made up to 500 ml. and analyzed as follows for HCl, $ClCH_2CH_2OH$, and $(ClCH_2CH_2)_2O$. HCl was titrated using methyl orange. $ClCH_2CH_2OH$ was detd. argentometrically: 2 *N* NaOH is added to the sample to give a concn. of 0.4 mole/l., heated to 60° 25 min., and acidified by HNO_3, after which titration with 0.1 *N* $AgNO_3$ and NH_4SCN in the presence of a little AmOH (to stabilize the endpoint) gives sufficiently accurate results. Steam distn. was used to sep. the di-Cl ether in the presence of $CaCl_2$, the oil, composed of the ether and $(ClCH_2)_2$, is sepd. and again distd. with steam, the vol. is measured and the mixt. washed with H_2SO_4 to ext. the ether, using a correction blank of 0.05 ml. The results of 7 expts. gave the av. value of $k'/k = 0.021$; application of a correction for the concurrent formation of $ClCH_2CO_2H$ gives 0.020. H_2O and $ClCH_2CH_2OH$ are approx. equally effective in their reaction with the primary complex of C_2H_4 with Cl_2. The reaction equation is useful for solving several related problems. If pure H_2O, instead of a $ClCH_2CH_2OH$ soln., is satd. with the gases, then $E_0 = 0$, and the equation is: $X = \frac{1}{2} \times k'/k \times E^2 = 0.0105\,E^2$; if the final $ClCH_2CH_2OH$ concn. is 1 mole/l., the di-Cl ether content will be 1% of the alc., while 2 mols./l. concn. will give 2%. G. M. Kosolapoff

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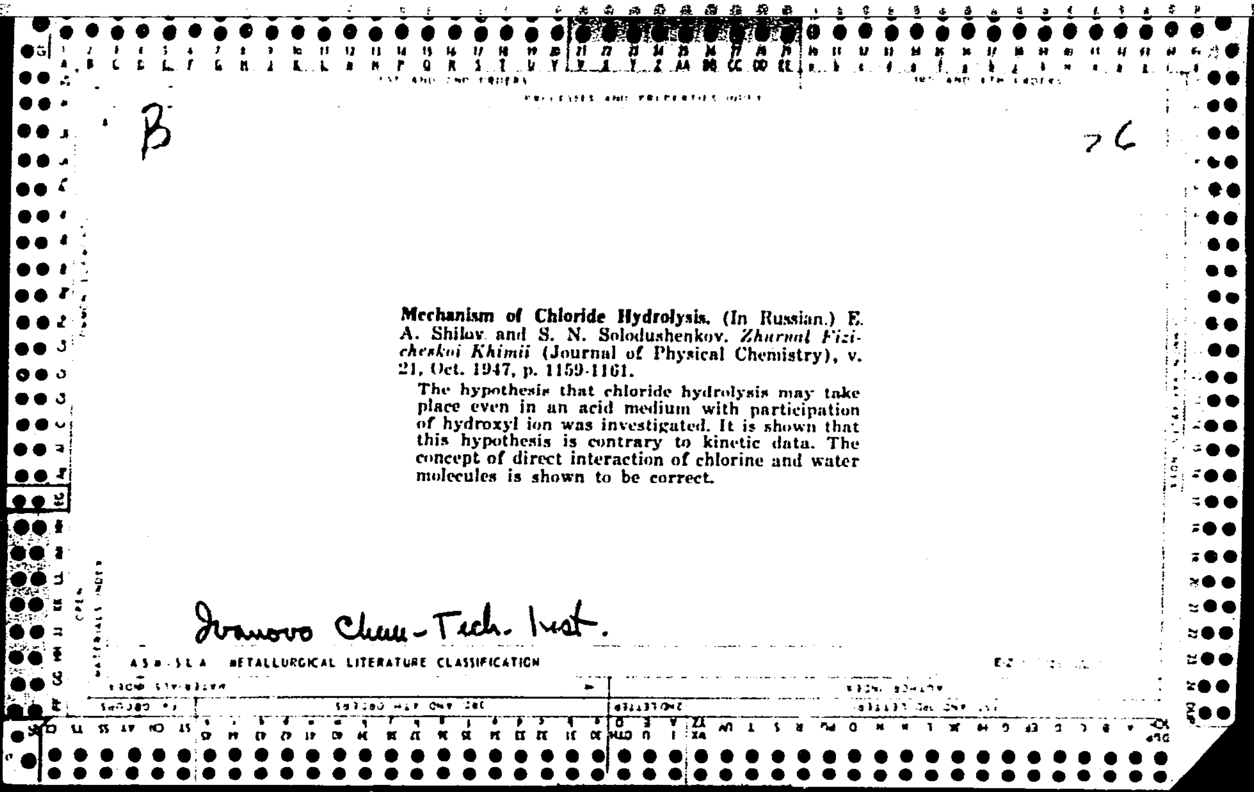
Benzyl 2- and 4-methoxy-1-naphthyl ketones and phenyl 2- and 4-methoxy-1-naphthyl diketones. S. I. Burmistrov and B. A. Shilov (Chem. Tech. Inst., Ivanovsk). *J. Gen. Chem.* (U.S.S.R.) 17, 1684–7(1947)(in Russian).—$PhCH_2CO_2H$ (41 g.) was heated on a steam bath 1 hr. with 21 g. PCl_3, the cooled mixt. treated with 40 cc. CS_2, and the soln. gradually added with ice-cooling to 55 g. $AlCl_3$ suspended in 140 cc. CS_2 contg. 48 g. 1-$MeOC_{10}H_7$; after 15 min. the mixt. was decompd. with ice and the org. layer distd. with steam; the residue was heated with soda soln. and the insol. matter on crystn. from EtOH gave 47% *benzyl 4-methoxy-1-naphthyl ketone*, m. 84°; *picrate*, m. 128°. This (7 g.) heated 2 hrs. to 140–50° with 4.4 g. SeO_2 in 15 cc. Ac_2O gave 80% *Ph 4-methoxy-1-naphthyl diketone*, m. 166° (from Me_2CO); this gives a quinoxaline on heating with o-$C_6H_4(NH_2)_2$, while oxidation with H_2O_2 in aq. pyridine gave BzOH and 4-methoxy-1-naphthoic acid, m. 236°; the latter acid treated with $SOCl_2$, then $PhNH_2$, gave the anilide, m. 220°. The diketone (1.2 g.) heated 1.5 hrs. to 100° with 1 g. o-$C_6H_4(NH_2)_2$ in 8 cc. pyridine and several drops of concd. HCl, gave *2-phenyl-3-(4-methoxy-1-naphthyl)quinoxaline*, m. 176° (from EtOH); *picrate*, red, m. 167° (from EtOH). The reaction of $PhCH_2COCl$ with 2-$MeOC_{10}H_7$ similarly gave *benzyl 2-methoxy-1-naphthyl ketone*, m. 74–6° (from EtOH); *picrate*, m. 101° (from EtOH). The ketone on oxidation with SeO_2 gave *phenyl 2-methoxy-1-naphthyl diketone*, m. 139° (from EtOH), which gives a red color with Na in EtOH soln., the color vanishing on shaking, then reappearing; oxidation gave 2-methoxy-1-naphthoic acid, m. 174° (decompn.).

G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION



B

7C

Mechanism of Chloride Hydrolysis. (In Russian.) E. A. Shilov and S. N. Solodushenkov. *Zhurnal Fizicheskoi Khimii* (Journal of Physical Chemistry), v. 21, Oct. 1947, p. 1159-1161.

The hypothesis that chloride hydrolysis may take place even in an acid medium with participation of hydroxyl ion was investigated. It is shown that this hypothesis is contrary to kinetic data. The concept of direct interaction of chlorine and water molecules is shown to be correct.

Ivanovo Chem-Tech. Inst.

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

PA 18/49T6

USSR/Chemistry - Argentometry Jul/Aug 48
Chemistry - Analysis, Volumetric

"The Use of Organic Liquids in Argentometric Titration," Ye. A. Shilov, Inst of Org Chem, Acad Sci Ukrainian SSR, Ivanovo Chem Eng Inst, 3 3/4 pp

"Zhur Analit Khimii" No 4

Shows that various insoluble alcohols, isoamyl, octyl, benzyl and cyclohexanol, can be used instead of nitrobenzene in volumetric determinations by Fol'gard's method. Many other ordinary liquids, which do not contain complex-forming groups, are almost or completely

[redacted]

18/49T6

USSR/Chemistry - Argentometry (Contd) Jul/Aug 48

ineffective as additives to conglomerate silver deposits. Submitted 3 Sep 47.

[redacted]

18/49T6

SHILOV, YE. A.

PA 68T38

USSR/Chemistry - Burets, Micro- **Feb 1948**

"The Improved 'Microburet' of P. M. Isakov," Ye. A. Shilov, 1 p

"Zhur Obshch Khim" Vol XVIII (LXXX), No 2

Brief article stating that P. M. Isakov's ideas concerning a micrometric screw are not at all new. Submitted 20 Jun 1947.

[redacted]

68T38

CA

10

The mechanism of carboxylation and of analogous reactions. E. A. Shilov and M. N. Bogdanov. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 1060-1(1948).—The conclusions of Gershzon (C.A. 39, 4595⁴) about the intramol. course of these reactions are invalid. Substances which split off PhNCO on heating can react with phenols, yielding the same anilides of HO acids as are obtained in rearrangements described by G. The only difference in the reactions of PhNCO itself is its tendency to polymerize, so that the anilide formation can occur only at temps. at which depolymerization of PhNCO is appreciable. The absence of cross-reactions is not a valid argument, for it is obscured by a large amt. of tarry by-products; furthermore, a cross-reaction between naphthoxides and salicylanilide of *p*-chlorobenzoic acid was observed. This can be best explained by preliminary loss of PhNCO, which then acts on the naphthoxide in preference to *p*-chlorophenoxide. Heating 4 g. PhNCO trimer and 4 g. NaOPh in a sealed tube 2 hrs. at 200°, followed by treatment with 3% NaOH, gave $CO(NHPh)_2$ (m. 236°) and 0.5 g. salicylanilide, m. 135° (from 50% AcOH); similarly, 5.4 g. 1-$NaOC_{10}H_7$ gave 3.2 g. 1-hydroxy-2-naphthanilide, m. 152°. Heating 5 g. PhOCONHPh (I) and 2.7 g. PhONa 2 hrs. to 190-200° gave $CO(NHPh)_2$ and 0.6 g. salicylanilide; 6.8 g. I and 3 g. 1-$C_{10}H_7ONa$ after 2 hrs. at 200-10° gave 0.6 g. 1,2-$HOC_{10}H_6CONHPh$ and no salicylanilide; 8 g. I and 5.8 g. 1-$NaOC_{10}H_7$ after 1.5 hrs. at 180° gave 2 g. 1,2-$HOC_{10}H_6CONHPh$, 2 g. 1-naphthol, and some tars. Heating *p*-ClC_6H_4ONa and PhNCO 1.5 hrs. at 200° gave 2-hydroxy-5-chlorobenzanilide, m. 207° (from EtOH). *p*-$ClC_6H_4O_2CNHPh$, m. 138-9° (from $COCl_2$ and *p*-ClC_6H_4OH, followed by treatment with $PhNH_2$), (4 g.) was converted to the Na deriv. in hot PhMe and this was heated 1.5 hrs. at 200°, giving 0.5 g. triphenylguanidine and 0.3 g. 2-hydroxy-5-chlorobenzanilide, m. 207°; heating 5.8 g. of the above Na deriv. in 25 ml. PhMe with 9.3 g. 1-$NaOC_{10}H_7$ 1.5 hrs. to 200° gave 0.6 g. 1,2-$HOC_{10}H_6CONHPh$, m. 152°, and no traces of 2-hydroxy-5-chlorobenzanilide could be found. The cross-reaction thus confirms the intermol. mechanism of the reaction.

G. M. Kosolapoff

Ivanovo Chem-Tech. Inst, Lab. Org. Chem

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Theory of sulfonation of aromatic amines. E. A. Shilov and A. N. Kurakin. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 18, 2002-3(1948). As shown in the preceding abstr., sulfonation of Me_2NPh by fuming H_2SO_4 gives about equal amts. of *m*- and *p*-sulfonates. This explodes the recent theory of Alexander (C.A. 41, 6218i) on the mechanism of sulfonation of aromatic amines. Even in oleum the equil. between Me_2NPh and its sulfate is such as to permit the existence of appreciable free amine, which orients the sulfo group to the para position; the salt, as well as the quaternary compd. (see preceding abstr.), naturally give the meta orientation. The meta sulfonation of primary and secondary amines also goes via the ammonium-salt route; the *o*- and *p*-isomers are formed via the sulfamic acids and the resulting $NHSO_3H$ group protects the NH_2 group from formation of ammonium-type salts. The complexes of amines with SO_3, due to their saltlike properties, should direct to the meta, and not to the ortho, para positions as suggested by Alexander, although a degree of dissocn. to free amine may permit the free amine reaction (see above).

G. M. Kosolapoff

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

SHILOV, YE.A.

E.A. Shilov and A.I. Sliadnev, Kinetics and mechanism of the reactions of active chlorine with organic compounds. VII. Oxidation of formic acid in acid solutions. Pp. 1312-21.

The rate of oxidation of formic acid by chlorine in acid water solution is determined by the equation

$$-\frac{d[Cl_2]}{dt} = K[Cl_2][HCO_2] + K^1 (Cl_2) [HCO_2H]$$

at 20°, $K = 295$, $K^1 = 0.028$; at 0°, $K = 28.5$, $K^1 = 0.0056$. The oxidation of formic acid in an acid environment proceeds through elementary chlorine and hereby differs from the oxidation of oxalic acid, where the active agent, even in the presence of chlorine, is hypochlorous acid.

Acad. of Sciences Ukranian S.S.R.
Inst. of Organic Chemistry, Kiev
Chemico-technological Inst., Ivanovo
March 3, 1948

SO: Journal of Physical Chemistry (USSR) 22, No. 11, 1948

SHILOV, E. A.

E. A. Shilov and A. N. Kurakin, On the theory of sulfonation of aromatic amines. p. 2092.

It is shown that the hypothesis by Alexander dealing with the mechanism of sulfonation of aromatic amines is based on inaccurate data in the literature. Some considerations concerning the actual course of the reaction of sulfonation are discussed.

Lab. of Organic Chemistry of the
Ivanov Chemico-Technological Inst.
August 7, 1947

SO: J. Gen. Chem. (USSR) 28, (80) No. 12, 1948

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2

The kinetic equations of the Cannizzaro reaction. K. A. Shilov and G. I. Kudryavtsev. *Doklady Akad. Nauk S.S.S.R.* 63, 681-4(1948).—Dismutation of m-$OHCC_6H_4SO_3Na$ (I) is of the 4th order, i.e. 2nd-order with respect to I and 2nd-order with respect to alkali. In aq. soln., at initial concns. 0.1-0.4 *M*, the 4th-order rate const., reduced to the ionic concn. 0.3 *M*, at 40, 50, and 60°, is k_4 = 0.49, 0.88, and 1.43 (moles/l., min.); in 8% alc., at 50°, k_4 = 0.41. There is a distinct pos. salt effect. Cannizzaro dismutation of 2-pyridinecarboxaldehyde (II) follows the 2nd order (1st-order with respect to II and 1st-order with respect to alkali); at 40°, in H_2O, k_2 = 0.0316, at 50°, in 48% alc., k_2 = 0.0175; no salt effect. The causes of the differences in the order of the reaction rate are unknown.

N. Thon

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

SHILOV, Ye. A. (Co-author)

See: YASNIKOV, A. A.

Yasnikov, A. A. and Shilov, Ye. A. - "The benzoin condensation of aldehydes with groups of type II", (Report), Soobshch. o nauch. rabotakh chlenov Vsesoyuz. khim. o-va im. Mendeleyeva, 1949, Issue 2, p. 8-9.

SO: U-4630, 16 Sept. 53 (Letopis 'Zhurnal 'nykh Statey, No. 23, 1949).

CA

10

The synthesis of 2-chloroethanol. VI. The theory of the Gomberg synthesis. E. A. Shilov. *Zhur. Priklad. Khim.* (J. Applied Chem.) 22, 734-46(1949); cf. *C.A.* 43, 3783i.—The Gomberg synthesis of $ClCH_2CH_2OH$ (I) (*C.A.* 13, 2309) is explained in the light of S.'s work. The concn. of I cannot exceed 1 mol./l. for 2 reasons: (*a*) the accumulation of HCl and I in the soln. shifts the homogeneous reaction in the direction of $(CH_2Cl)_2$ (II) and $(ClCH_2CH_2)_2O$; and (*b*) the appearance of slightly sol. chlorides causes a reaction in the org. layer which increases the formation of side-reaction products. In order to force the homogeneous reaction in the direction of an increased yield of I, it is necessary to remove all Cl^- from the soln. From this point, the theory can be used to calc. the yields of the reaction products for industrial design purposes. In order to inhibit reaction in the org. layer, II should be removed from the reaction mixt. to increase the partial pressure of the Cl and decrease the temp. A new technique which is introduced by the theory is to allow the C_2H_4 and Cl to be mixed in gaseous form within the soln., which is in accord with good technology. This new point of view requires the consideration of certain points of design for industrial units. It is also possible to consider satg. the concd. HOCl soln. with C_2H_4, which requires effective dispersion of the C_2H_4 in the soln. and an increase in pressure. The 1st requirement is self-evident but the 2nd is met with the problem of the deposition of solid Cl hydrates. The problem may be solved, however, by suspending the Cl hydrate in H_2O which has been satd. with compressed C_2H_4. Thus, after a few min., a soln. of I having a concn. of 1 mol./l. (or 8%) was obtained. The method could be easily adapted to industrial use.

Paul W. Howerton

1951 Inst. Org. Chem., AS UkrSSR

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CA

10

Catalytic effects in the Cannizzaro reaction. G. I. Kudryavtsev and E. A. Shilov. *Doklady Akad. Nauk S.S.S.R.* 64, 73-6(1949).—(1) Acceleration of the Cannizzaro dismutation of BzH (I) and *m*-$OHCC_6H_4SO_3Na$ (II) by peroxides is illustrated by the following rate consts., *k*, at 50° (3rd-order for I, 4th-order for II): I, initial concn. 0.55 *M*, in 40% alc., the NaOH 0.27 *M*, without and with 0.0002 *M* Bz_2O_2, *k* = 0.0016 and 0.0021, resp.; I, initial concn. 0.28 *M*, in 50% dioxane, without and with Bz_2O_2, 0.00059 *M*, *k* = 0.0019 and 0.0040, resp.; II in H_2O, initial concns. of II and of NaOH 0.088 *M*, ionic concn. 0.176 *M*, with H_2O_2 0, 0.00005, 0.0001, and 0.0018 *M*, *k* = 0.57, 0.69, 0.82, and 1.03. (2) Dismutation of I is also accelerated by metallic Ag, Co, Ni, and Cu, in decreasing order of effectiveness. Hydroxides of Cu, Ni, Co, Fe, and Mn are inactive, and so is metallic Fe. The activity of Ag_2O is due to its reduction to Ag. The Cannizzaro reaction of *o*-HOC_6H_4CHO is accelerated by metallic Ag, Ni, and Co, not by Fe. The catalytic effect of metals is attributed to dehydrogenation.

N. Thon

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ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

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Spatial orientation of the addition reaction to a multiple bond. I. V. Smirnov-Zamkov and B. A. Shilov. *Doklady Akad. Nauk S.S.S.R.* 67, 671-4(1949).—The product of the addn. of HBr to MeO$_2$CC:CCO$_2$Me (I) depends on the solvent. In glacial AcOH, C$_6$H$_{14}$, MeNO$_2$, and in pure liquid phase, methyl bromomaleate (II) and bromofumarate (III) are formed in approx. equal amts. In C$_6$H$_6$, over 90% of the product is III. Concn. and temp. have no effect on the orientation of the addn., nor has the presence of peroxides or antioxidants. LiBr or HgBr$_2$ shifts the reaction in favor of III. The rate of the reaction is of the 3rd order, $-d[HBr]/dt = k[I][HBr]^2$, with k (in mols./l. min.) = 0.21 (at 20° in glacial AcOH), 1.80 (at 20° in C$_6$H$_6$), and 5200 (at 0° in C$_6$H$_{14}$). In the presence of LiBr, the rate follows $-d[HBr]/dt = k'[I][HBr][Br^-]$, with $k' = 0.91$ (at 20°). Peroxides and antioxidants have no effect on the rate; Ac$_2$O slows it down; H$_2$O in large amts. slows it down, in small amts. accelerates it. The reaction is conceived as proceeding over an intermediate addn. complex between I and HBr, with a pos. charge located at one of the triple-bond C atoms, a neg. charge at the Br atom of the HBr mol. bound to the other C atom through its H atom. This complex reacts further with Br$^-$ which is bound at the positively charged C atom, i.e. in a trans position, or, less energetically, with a 2nd HBr mol.; this stage is the rate-detg. step. On the other hand, a HBr mol. can also approach the primary intermediate complex from its neg. end, in which case the H atom of the HBr mol. will be bound at the negatively charged Br resulting in an addn. in the cis position. The nature of the solvent dets. mainly the formation of the primary complex.

N. Thon

ASM-SLA METALLURGICAL LITERATURE CLASSIFICATION

BA

BII-6

"Danger zone" of chlorine bleaching. E. A. Shilov and A. A. Yasnikov (*Tekst. prom.*, 1950, No. 11, 35—38).—The "danger zone," in which max. fibre damage occurs in hypochlorite bleaching, is in the pH range 6—8. The rates of oxidation of lactic and D-gluconic acids, starch, EtOH, and cellulose by HOCl all show a sharp max. at pH 6—8. By analogy with the mechanism of oxidation of saturated alcohols by HOCl, it is supposed that hydroxy-acids, polyhydric alcohols, and cellulose are oxidised with the intermediate formation of unstable hypochlorite esters in 2 stages: (1) $\cdot CH\cdot OH + HOCl \rightarrow \cdot CH\cdot OCl + H_2O$; $\cdot CH\cdot OCl + OH' \rightarrow \cdot CO + H_2O + Cl'$. At low pH, when much HOCl is present and [OH'] is low, the reaction rate is determined by stage (2) and increases approx. ∝ [OH']; in the alkaline region it is mainly determined by stage (1), and depends on [HOCl]; thus it reaches a max. at pH ~7. Bleaching proper, *i.e.*, the destruction of coloured compounds, proceeds by a different mechanism and the rate falls with increase of pH. From the data of Clibbens and Ridge (B., 1927, 471) on the effect of pH on cellulose oxidation it is concluded that the range pH 8·5—10 avoids the "danger zone" but maintains an adequate rate of bleaching. The range pH 2—3·5 also avoids the danger zone and gives a max. bleaching rate; this suggests the practical possibility of chlorine-water bleaching.

E. B. UVAROV.

-A

2

New determination of the electrolytic dissociation constant for hypobromous acid. E. A. Shilov (Inst. Org. Chem., Kiev). *Zhur. Fiz. Khim.* 24, 703-6(1950).—Skrabal's electrometric titration of HOBr is disputed. The new detn. of the electrolytic dissocn. const. for HOBr by electrometric titration with a glass electrode was $K = 2.1 \times 10^{-9} \pm 0.1 \times 10^{-9}$ at 22° and ion concn. = 0.1-0.02 *M*. Paul W. Howerton

CA

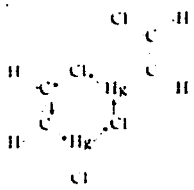
2

Kinetics and mechanism of the oxidation of nitrous acid by hydrogen peroxide. E. A. Shilov and Z. S. Stepanova (Chem.-Tech. Inst., Ivanovo). *Zhur. Fiz. Khim.* 24, 820-31(1950).—The reaction rate of $NaNO_2$ with H_2O_2 in the presence of HNO_3 (concn. 0.0004–0.0012 *M*) was measured with and without neutral salts (KNO_3, Na_2SO_4, $NaClO_4$). The kinetic equation is: $-d[H_2O_2]/dt = F_0k[H_2O_2][HNO_2]^2 + Fk'[H_2O_2][HNO_2][H^+]$. The second term may be written: $FKk'[H_2O_2][HNO_2]^2/[NO_2^-]$. The parameters F_0 and F depend on the salt effect, and K is the dissocn. const. of HNO_2. When the nitrite concn. changes from 0.001 to 0.5 *M* and the neutral salt concn. is varied between 0 and 0.5 *M*, *FK* changes from 1 to 3 and F_0 from 1 to 1.3. At 20°, $k = 2.3 \times 10^3$ and $k' = 1.48 \times 10^4$ (units: g. mol./l. min.). The temp. coeff. of the reaction corresponding to the const. *k* is 2.43 between 0 and 10° and 2.2 between 10 and 20°. For the reaction with const. *k'*, the temp. coeff. is 2.46 and 2.31 in the same temp. intervals. The kinetics suggest the following sequence of reactions: (I) $H_2O_2 + HNO_2 \rightleftharpoons HOONO + H_2O$; (IIa) $HOONO + HNO_2 = HNO_3 + HNO_2$ or (IIb) $HOONO + H^+ = H^+ + HNO_3$. Equil. I is shifted rapidly, whereas *IIa* and *IIb* are the rate-detg. steps corresponding, resp., to the 1st and 2nd terms of the kinetic expression. Peroxynitrous acid HOONO is the active intermediate in the reaction. M. Boudart

C A

10

Theory of the formation of *cis*-chlorovinylmercury chloride from acetylene and mercuric chloride. I. V. Smirnov-Zamkov and E. A. Shilov (Inst. Org. Chem., Acad. Sci. Ukr. S.S.R., Kiev). *Doklady Akad. Nauk S.S.S.R.* **73**, 723-5(1950). At 100°, formation of *cis*-CHCl:CH-HgCl (I) from C_2H_2 and solid $HgCl_2$ involves an induction period of approx. 1 hr. That induction period is shortened very markedly by advance addn. of some I. Addn. of the trans isomer has no accelerating effect; on the contrary, it inhibits somewhat the formation of I. That the difference of the effects of the cis and the trans isomers is not due to the lower melting temp. of I is demonstrated by the fact that at 124°, too, only an addn. of I suppresses the induction period and accelerates the reaction, whereas the same amt. (5%) of the trans isomer has a marked inhibiting action. I is the only product in the absence of Cl⁻ ions; in their presence, the reaction is trimol. and its product is the trans isomer. Formation of I is interpreted by a mechanism involving a 6-membered cyclic intermediate formed from C_2H_2, $HgCl_2$, and I, of the structure II, which decomp. into 2 I.



(II)

The trans isomer, being less polarizable in its HgCl group, is evidently not sufficiently active at 100-24° to form the cyclic intermediate. N. Thon

SHILOV, Ye. A.

PA 174T7

USSR/Chemistry - Bromine Addition Jan/Feb 51

"Stereochemistry and Mechanism of Addition of Bromine by the Tertiary Bond," Ye. A. Shilov, I. V. Smirnov-Zamkov, Inst Org Chem, Acad Sci Ukrainian SSR

"Iz Ak Nauk SSSR, Otdel Khim Nauk, No 1 pp 32-41

Shows addn of Br to dimethyl ester of acetylenedicarboxylic acid proceeds by either radical or donor-acceptor mechanism. Radical reaction in various soln always yields cis- and trans-dibromides in approx equal proportions. Donor-acceptor reaction, observed in expt with admixt, yields only trans-isomer (dibromfumaric ester).

LC 174T7

CA

70

Hypothesis of quasicomplex state and associated problems of theory of organic transformations. E. A. Shilov. *Zhur. Obshchei Khim.* (*J. Gen. Chem.*) **21**, 2084-93(1951). Polemical criticism of Nesmeyanov's concept of quasicomplex compds. (cf. *C.A.* **41**, 3046e). It is suggested that isomeric and tautomeric substances are the sole possible structures and the quasicomplex compds. are merely one aspect of general donor-acceptor electromeric electron transfer. **Reply.** A. N. Nesmeyanov. *Ibid.* 2093-100. G. M. K.

CA

6

A paper of Abel concerning pernitrous acid. E. A. Shilov (Inst. Org. Chem. Acad. Sci. Ukr. S.S.R., Kiev). *Zhur. Fiz. Khim.* 25, 1137(1951).—The theoretical considerations of Abel (*C.A.* 44, 1355*g*), who ascribes to N_2O_4 the role of active intermediate in the oxidation of HNO_2 by H_2O_2 lead to a kinetic equation which is not compatible with that found experimentally by S. and Stepanova (*C.A.* 45, 4121*d*), who ascribe the same role to pernitrous acid.

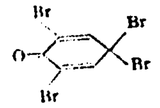
Michel Boudart

1952

CA

10

The structure of tribromophenol bromide and some data on the theory of its formation. A. A. Yasnikov and E. A. Shilov. *Doklady Akad. Nauk S.S.S.R.* **78**, 925-8(1951).—The literature is reviewed (7 references). An aq. suspension of 2,4,6-$Br_3C_6H_2OH$ (I) was mixed with radioactive Br water (active Br), the ppt. recrystd. from CCl_4, taken up in C_6H_6, and the soln. divided; 1 part was reduced with aq. NaI-$Na_2S_2O_3$, the other was untreated, and samples of both were dried on filter paper and their activity detd. The fraction of residual activity was found to depend on the method of mixing the reagents in making the tribromophenol bromide (II). If the suspension of I is added to Br water, then upon reduction of the isolated product somewhat over 50% of the initial activity is retained, but if the addn. is done in reverse, the product on reduction retains only 25% of the activity, indicating exchange of all 3 Br atoms; an increase of reagent ratio can lower the activity still further. II in aq. suspension does not exchange Br with Br water or NaBr, but slow exchange occurs with concd. HBr in aq. or C_6H_6 media. The exchange of Br between I and II is very slow in aq. suspension, but is accelerated by a transfer agent like pyridine. Apparently the exchange occurring during the formation of II is explained by the "active" state of Br during the reaction. Hence, addn. of I to Br water affords the only safe approach to the structure of II. The above results show that II has the structure of a quinone bromide, and not that of a hypobromite. I does not react with Br in CCl_4 or AcOH, but addn. of a H acceptor (pyridine or H_2O) gives an immediate ppt. of II; probably the H is detached from the HO of the phenol and the product assumes the final structure:



G. M. Kosolapoff

CA

2

Kinetics of the addition of hypochlorous acid to molecules with a little-active double bond. B. A. Shilov, G. V. Kupinskaya, and A. A. Yasnikov (Inst. Org. Chem., Acad. Sci. Ukr. S.S.R., Kiev). *Doklady Akad. Nauk S.S.S.R.* 81, 435-8(1951).—Addn. of HOCl to $Me_2(CH_2{:}CHCH_2)NClO_4$ (I) is slow enough for a kinetic study. The product of the addn. (irrelevant for the kinetics) is taken to be $Me_2(CH_2OHCHClCH_2)NClO_4$, i.e. the addn. is anti-Markovnikov, contrary to Schmidt (*Ann. Chem.* 337, 44(1905)). In the absence of HCl, the kinetics of the reaction is represented by $-dc/dt = k_1[I][HOCl]^2$, where c = concn. of active Cl, with k_1 = 3.5 at 25° and 1.7 at 15° (units mole/l., min.). The 2nd order in HOCl indicates that the reaction proceeds over $[Cl_2O] \rightleftarrows K'[HOCl]^2$. If the pH of the soln. is raised through addn. of alkali or buffers, the reaction becomes slower and comes practically to a halt at pH = 8.1. Evidently, the ClO^- ion does not react with I, and its catalytic effect on the formation of Cl_2O from HOCl is unimportant, as this step is not limiting anyway. In expts. at higher pH, the analytical active-Cl concn. c is expressed by [HOCl] through $c = [1 + (K/[H^+])][HOCl] = q[HOCl]$, where K is the electrolytic dissocn. const. of HOCl; this gives $-dc/dt = k_1[I]c^2/[1 + (K/[H^+])]^2 = (k_1/q^2)[I]c^2$. The const. k_1 remains satisfactorily const. at pH 4.9-8.1, with [I] = 0.05-0.1, c = 0.005-0.02, q = 1-36, $K = 3.8 \times 10^{-8}$. The calcns. bear out the assumption of Cl_2O as the active agent of the reaction. In the presence of HCl (not less than 0.1 *M*), addn. of HOCl is accelerated very considerably, which indicates Cl_2 mols. as the active agent; there is no reason to doubt that the product of the addn. remains the same. The rate is slow enough for measurement only at as low as 0°; at that temp., the rate const. defined by $-dc/dt = k_2[I][Cl_2]$ is $k_2 = 40 \pm 3$ (mole/l., min.). The values of k_1 and k_2 permit comparison of the activities of Cl_2O and Cl_2, with the aid of the equil. $[Cl_2O]/[HOCl]^2 = K' = 0.00355$ at 0°, and k_1 = 0.6 extrapolated to 0°. This gives $-dc/dt = 0.6[I][HOCl]^2 = (0.6/0.00355)\ [I][Cl_2O] = 170[I][Cl_2O]$, i.e. Cl_2O is 4.2 times as active as Cl_2 with respect to addn. to a double bond.

N. Thon

2

CA

Acyl hypochlorites and the chlorine cation as chlorination agents of unsaturated organic compounds in aqueous solution. K. A. Shilov and G. V. Kupinskaya (Inst. Org. Chem., Acad. Sci. Ukr. S.S.R., Kiev). *Doklady Akad. Nauk S.S.S.R.* 81, 621-4(1951); cf. preceding abstr.—The accelerating effect of carboxylic acids on the addn. of HOCl to a double bond, in a pH range high enough (above 3.5) for a direct addn. of Cl_2 to be insignificant, is attributed to intermediate formation of highly active acyl hypochlorites, according to $HOCl + HOOCR \rightleftarrows ClOOCR + H_2O$. That this catalytic action is due to the undissocd. carboxylic acid, not to the carboxylate anion, follows from the fact that it disappears altogether at a pH around 7.5, where the amt. of free HOCl is still high, but the concn. of free carboxylic acid insignificant. In the chlorination of trimethylallylammonium perchlorate (A) in the presence of an undissocd. carboxylic acid (HAn), the rate law is $-dc/dt = k_1A[HOCl]^2 + k_1'A[HOCl][HAn]$, where c = anal. concn. of active Cl in mole/l., and $k_1 = 3.5$ at 25° (time in min.). At const. pH and const. A and [HOCl], the plot of $-dc/dt$ as a function of [HAn] should be a straight line. This is confirmed by the following exptl. data at 25°, with $A = 0.1$ M (initial c, carboxylic acid [concn. M], pH, [HAn], k_1'): 0.005, AcOH [0.1 and 0.2], 3.64, [0.05 and 0.1], 0.44 and 0.46; 0.01, $o\text{-}C_6H_4(CO_2H)CO_2^-$ [0.025, 0.05, and 0.1], 5.22, [0.0136, 0.0369, and 0.0534], 1.40, 1.46, and 1.40; 0.01, $ClCH_2CO_2H$ [0.056, 0.3, and 0.75] 3.6, [0.0084, 0.040, and 0.11], 3, 4.1, and 4.5. Phthalic acid at pH 3.86 accelerates more strongly than at pH 5.22. At the higher pH, the catalyzing agent is the monoion $o\text{-}C_6H_4(CO_2H)CO_2^-$; at pH 3.86, it is apparently $o\text{-}C_6H_4(CO_2H)_2$, concn. [HAn_1]. In the rate equation, there is an addnl. term $k_1''A[HOCl][HAn_1]$, with k_1'' (av.) = 21. The values of k_1' and k_1'' evidently increase with the electrolytic dissocn. const. of the carboxylic acid, but there is no direct proportionality. In the presence of HCl, in the amt. of 10% of the HOCl, and of a strong inorg. acid (HNO_3 0.5-1.5 M, or H_2SO_4 0.5-1.0 M), the rate const. k_1 defined by $-dc/dt = k_1A[Cl_2]$ remains very close to 40, i.e. to the value previously found with small amts. of HCl. There are no indications of the presence of a Cl^+ cation.

N. Thon

SHILOV E.A

Theory of the structure and reactivity of organic compounds. E. A. Shilov. *Ukrain. Khim. Zhur.* 18, 123-40 (1952)(in Russian).—A review of modern theories of structure and reactivity, with particular attention to resonance and mesomerism. 22 references. C. M. K.

Shilov, E. A.

5

Chemical Abst.
Vol. 48 No. 9
May 10, 1954
General and Physical Chemistry

③ Chem

Kinetics and mechanism of reactions of active chlorine with organic compounds. VIII. Oxidation of formic acid in nearly neutral and alkaline solutions. E. A. Shilov, A. I. Slyadnev, and G. V. Kupinskaya. *J. Gen. Chem. U.S.S.R.* 22, 1641-7(1952)(Engl. translation).—See *C.A.* 47, 2582*b*.
H. L. H.

SHILOV, E. A.

Kinetics and mechanism of reactions of active chlorine with organic compounds. IX. Oxidation of glycolaldehyde and *d*-glucose. E. A. Shilov and A. A. Yasnikov. *Ukrain. Khim. Zhu*~~r. 18, 595-610~~(1952)(in Russian); cf. *C.A.* 48, 4944*b*.—Oxidation of glycolaldehyde (I) and *d*-glucose (II) by active Cl in aq. soln. was examined. The variation of the rate with pH is such that the state of HOCl (pH 4–5) appears to correspond to the slowest reaction. The oxidation rate rises on addn. of HCl or alkali. In the range pH 5–13.5 the rate of oxidation increases with pH but in a complex manner. In pH range 5–9.5 the oxidation of I and II follows: $-(dc/dt) = kC[HOCl]a$, where C is concn. of the hydroxy deriv., and a is concn. of HO ions. Value of k declines with increase of pH and is av. 15×10^6 for I and 4×10^6 for II (time in min.). At pH 10-13.5 the rate of oxidation of I and II is given best by $-(dc/dt) = k_0C$; where k_0 for I goes from 7.5×10^{-4} at pH 10 to 2.5×10^{-1} at pH 13.5; for II these are 2.5×10^{-4} and 4×10^{-4}, resp. In acid medium the active agency is Cl; in neutral or weakly alkaline medium it is HOCl the latter case proceeding through two steps. At high pH the enolate form appears to be oxidized. **X. Oxidation of hydroxy acids.** *Ibid.* 611-24.—Oxidation of lactic acid (I) and *d*-gluconic acid (II), as well as preliminary study of pyruvic acid (III) was examd., at 25° in aq. soln. The rate of oxidation of I, II, and III by active Cl is very low in HCl, but rises with increase of pH rapidly, reaching max. rate at pH 7, after which it steadily declines. The rate of oxidation in descending order is: I, II, III. With deficiency of HOCl, I is oxidized to chloropyruvic acid, while II gives 2-oxogluconic acid. In the mid-range of pH values the rate of oxidation follows $-(dc/dt) = k_2AC$, where A is concn. of the org. acid, C is concn. of active Cl, k_2 a specific constant. Max. k_2 for I at pH 7 is 1.4, for II 0.3 (time in min.). Examn. of the kinetic data (given graphically) indicates that the active agent in mid-range of pH is HOCl, while HO ion is to some extent a catalyst. Cl and CCl$^-$ are relatively weakly active. The mechanism of the oxidation appears to include formation of an ester of HOCl, which is transformed into a carbonyl compound by loss of HCl. Similar considerations are probably true for reactions of alcs. and carbohydrates.

G. M. Kosolapoff

USSR/Chemistry - Chlorination 11 Jun 52

"Chlorine Cation as a Chlorinating Agent in Aqueous Solution," Ye. A. Shilov, Act Mem, Acad Sci Ukrainia SSR Inst of Org Chem, Acad Sci Ukrainian SSR

"Dok Ak Nauk SSSR" Vol LXXXIV, No 5, pp 1001 - 1003

De la Mare, Hughes, and Vernon (Research, Vol III, 192, 242, 1950), concluded from their work that chlorination with hypochlorous acid in aq soln takes place with the formation of chlorine cations. This is contradicted by the work of the present author, who established that reaction with the chlorine

223T21

cation does not play a significant role in the overall chlorination reaction for hydrogen ion concns below 1M.

223T21

SHILOV, YE. A.

Shilov, E.A.

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Problemy mekhanizma organicheskikh reaktsii (Problems in Mechanism of Organic Reactions). Edited by E. A. Shilov. Kiev: Izdatel. Akad. Nauk Ukr. S.S.R. 1953. 855 pp.

CH

SHILOV E.A.

USSR.

The kinetics of the oxidation of nitrous acid with hydrogen peroxide. E. A. Shilov (Inst. Org. Chem., Acad. Sci. Ukr. S.S.R., Kiev). *Zhur. Fiz. Khim.* 27, 1103-5(1953); cf. *C.A.* 45, 4121*d*.—A criticism of work reported by Halfpenny and Robinson (*C.A.* 46, 6026*c*; 47, 1077*d*) on the oxidation of HNO_2 with H_2O_2. J. Rovtar Leach

SHILOV, E.A.

**Mechanism of rearrangements of aromatic amino- and
hydroxysulfonic acid salts.** E. A. Shilov, M. N. Bogdanov,
and A. E. Shilov. *Doklady Akad. Nauk S.S.S.R.* 92,
93–6(1953).—The mechanism of direct sulfonation of
aromatic compds. by H_2N and HO sulfonic acids is dis-
cussed. In media with a high level of acidity, a mode of
migration of the SO_3H may change to a hydrolytic one,
which is connected with isotopic exchange. In the present
work S^{35} labeling was employed: a mixt. of S^{35}-labeled
Na_2SO_4 with ordinary naphthionate (or other salts) was
allowed to react and the test result interpreted by the
translocation of S^{35}. If the rearrangement takes place by
hydrolysis, the resulting H_2SO_4 or its salt will yield radio-
active sulfonate. If the rearrangement of the sulfonate is
intramol., the product is inactive. Although the systems
were heterogeneous, the reaction took place readily. The
results are summarized below. Na naphthionate and $C_{10}H_8$
in 3.5 hrs. at 100° gave 51% 1,2-salt, with 3% S exchange;
with 1-$C_{10}H_7NH_2$ in 2 hrs. at 180–200°, 60–90% 1,2-H_2N-
$C_{10}H_6SO_3Na$ was obtained with 5–10% S exchange; with
1-$C_{10}H_7NH_2$ in the presence of Na_2CO_3 no 1,2-salt formed
and no S exchange took place; 1-$C_{10}H_7OH$ in 4 hrs. at 190°
formed 35% 1,2-$HOC_{10}H_6SO_3Na$ with 4% S exchange.
Naphthionic acid and 1-$C_{10}H_7NH_2$ in 3 hrs. at 180° gave
45% 1,2-salt and 74% S exchange. 1-$C_{10}H_7NHSO_3Na$ and
$C_{10}H_8$ in 2 hrs. at 150° in the presence of 1-$C_{10}H_7NH_2$ and
H_2SO_4 gave 60% 1,2- and 7% 1,4-salt with much S ex-
change; if H_2SO_4 were omitted, 1.3 hrs. at 180° gave 67%
1,2-salt and 5% S exchange; $C_{10}H_8$ and 1-$C_{10}H_7OH$ gave
73% 1,2-$HOC_{10}H_6SO_3Na$ with 2% S exchange. Na sulfani-
late and 1-$C_{10}H_7NH_2$ in 3 hrs. at 193° gave 90% 1,2-salt
and 5% S exchange; addn. of Na_2CO_3 gave 0% 1,2-salt and
no S exchange. Sulfanilic acid and 1-$C_{10}H_7NH_2$ in 3 hrs.
at 190° gave 42% 1,2-salt with 38% S exchange. 2,1-
$H_2NC_{10}H_6SO_3Na$, the free acid, and 1,4-$HOC_{10}H_6SO_3Na$
gave a similar distribution of products. It is readily seen
that in many cases the SO_3H group migrates without
hydrolysis or S exchange, or at most with a small extent of
exchange. However, naphthionic acid and 2,1-H_2NC_{10}-
H_6SO_3H produce 45–90% S exchange. With 1,4-HO-

$C_{10}H_6SO_3Na$ and 1-$C_{10}H_7NHSO_3H$, the extent of the exchange is detd. by the acidity of the mixt., a more acidic medium promoting S exchange. Thus the process can be described as follows. A proton adds to the $H_2NC_{10}H_6SO_3Na$ a at the S-carrying C atom, forming a quinonoid structure, which then sulfonates another mol. of an amine or a naphthol. While 1-$C_{10}H_7NH_2$ facilitates the reaction, it is not essential. In the absence of the amine, transulfonation yields a disulfonate and a free $C_{10}H_7NH_2$, after which the above scheme is operative.

G. M. Kosolapoff

SHILOV, E.A.

4

/ Nucleophilic addition of hydrogen halides to some acetylenic derivatives. E. A. Shilov and A. B. Shilov. *Doklady Akad. Nauk S.*[illegible]5(1953).—In the addn. of HCl to $(:CCO_2Me)_2$ solns. of LiCl in AcOH form HCl adducts more rapidly than solns. of HCl alone under comparable conditions. The reaction yields di-Me chlorofumarate which does not add HCl under these conditions; thus the LiCl reaction also yields AcOLi. The addn. of LiCl in AcOH follows the equation: $-(dC/dt) = k_2AC$, where A is the concn. of the acetylenic ester and C that of LiCl; $k_2 = 3.4 \times 10^{-4}$ moles/l. min. at 30° and 26×10^{-4} at 50°. With free HCl the reaction is also of 2nd order but k_2 at 30° is 0.9×10^{-4}. When both HCl and LiCl are present they react independently of each other and a summational rate prevails. Strong acids, such as Cl_3CCO_2H, do not affect the rate of the LiCl reaction, but addn. of H_2O (up to 5%) accelerates the addn. of LiCl by some 50%. Undissocd. mols. of $(:CCO_2H)_2$ in aq. soln. also react almost equally rapidly with NaCl and HCl, thus showing that the rate of the over-all reaction is limited by the reaction of the Cl ion. Neither the neutral nor the acid salt of the acid reacts with aq. or AcOH solns. of the chlorides. Bromides and iodides are more active: LiBr in AcOH reacts with the ester 5 times as rapidly as LiCl; HI adds (from KI soln. in 80% AcOH) some 280 times as rapidly as HCl from LiCl soln. Thus the addn. of HCl from the salt soln. initiates with a nucleophilic attack of LiCl on the acetylenic link, followed by reaction of a mol. that contains active H but the 2nd reaction is much slower. The nucleophilic nature is shown by the fact that replacement of Ac by H or Ph lowers the rate of reaction of the acetylene deriv.; HC:CCO₂Me is less reactive, while PhC:CCO₂Me is even less reactive. The kinetic data are given in tables. G. M. K.

⑥

SHILOV, Ye.A.

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

Name	Title of Work	Nominated by
Shilov, Ye.A.	"Investigation of the Theory of Active Chlorine with the Aid of Organic Compounds"	Academy of Sciences Ukrainian SSR

SO: W-30604, 7 July 1954

SHILOV, Ye.A.; MOSPAN, V.S.

Dichlorofumaric acid and some of its derivatives. Ukr.khim.zhur. 20 no.1:35-38 '54. (MLRA 7:3)

1. Institut organicheskoy khimii Akademii nauk USSR. (Fumaric acid)

SHILOV, YE.A.

SHILOV, A.Ye.; SHILOV, Ye.A.

Research in the theory of nucleophile additions. Part 1. Kinetics of the addition of hydrogen chloride and analogous compounds to some acetylene derivatives. Ukr.khim.zhur. 20 no.1:39-52 '54. (MLRA 7:3)

1. Institut organicheskoy khimii Akademii nauk USSR.
(Hydrogen chloride) (Acetylene derivatives)

SHILOV, Ye.A.; SHILOV, A.Ye.

Studies in the theory of nucleophilic additions. Part 2. Kinetics of the chlorination of the dimethyl ester of acetylenedicarboxylic acid. Ukr.khim.zhur. 20 no.3:279-281 '54. (MLRA 7:8)

1. Institut organicheskoy khimii Akademii nauk USSR.
(Chlorination) (Acetylenedicarboxylic acid) (Esters)

SHILOV, Ye.

SAVINOV, B.; SHILOV, Ye.

In the Council for the Ukrainian State and Kiev Departments of the Mendeleev All-Union Chemical Society. Ukr.khim.zhur. 20 no.3:340 '54.
(Ukraine--Chemistry) (Chemistry--Ukraine) (MLRA 7:8)

Shilov, E.A.

USSR/Chemistry - Physical chemistry

Card 1/1 Pub. 147 - 22/27

Authors : Shilov, E. A., Yasnikov, A. A.

Title : Regarding the structure of isomeric pentachlorophenol chlorides

Periodical : Zhur. fiz. khim. 28/9, 1680-1681, Sep 1954

Abstract : Comments, on the report by P. P. Shorygin and M. I. Gostev stating that low-melting isomer of pentachlorophenol chloride has a structure similar to that of hypochlorous acid esters, are presented. The use of marked Cl, for the purpose of determining the structure of isomeric pentachlorophenol chlorides, is recommended. Four USSR references (1950-1954).

Institution : ...

Submitted : June 14, 1954

ONIKUL, Ya.Ye., inzhener; STRASHUN, K.Z., inzhener; ROMANOVSKIY, V.P., kandidat tekhnicheskikh nauk, dotsent; SHILOV, V.S., inzhener, retsenzent; VAYNTRAUB, D.A., inzhener, redaktor

[Stamping non-metallic materials] Shtampovka nemetallicheskikh materialov. Pod obshchei red. V.P.Romanovskogo. Moskva, Gos. nauchno-tekhn. izd-vo mashinostroit. lit-ry, 1955. 56 p. (Bibliotechka shtampovshchika, no.8) (MLRA 9:12)

(Sheet-metal work)

SHILOV, E. A.

3

✓ Donor-acceptor mechanism and its significance in kinetics of heterolytic reactions. E. A. Shilov. *Voprosy Khim. Kinetiki, Kataliza i Reaktsionnoi Sposobnosti, Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 1955, 749-56.—It is suggested that many heterolytic reactions in solns. can be readily treated by the electron-donor-acceptor concept. Several reactions of halides are thus briefly discussed. 14 references. G. M. Kosolapoff

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NA

MET

SHILOV, E.A.

USSR/ Chemistry - Organic chemistry

Card 1/1 Pub. 116 - 10/25

Authors : Shilov, E. A., and Vaynshteyn, F. M.

Title : The migration of sulfo group in aromatic sulfo-acids

Periodical : Ukr. khim. zhur. 21/1, 58-65, 1955

Abstract : The regrouping of p- and o-toluenesulfonic acids was investigated in the presence of radioactive sulfuric acid at 120 and 126° and at different reagent ratios. It was established that the S^{35} converts with measurable speed from the radioactive sulfuric acid into reaction products. The forming regrouping products (o- and p-isomers) show a high radioactivity already at the start of the reaction. The data obtained indicate that the regrouping of p- and o-toluenesulfonic acids takes place almost exclusively according to the intermolecular hydrolytical mechanism. Eleven references : 2 USSR, 5 German, L Swiss, 2 English and 1 USA (1870-1953). Graphs.

Institution : Acad. of Sc., Ukr-SSR, Institute of Organic Chemistry

Submitted : July 23, 1954

Lc. I P

5

Theory of the Kolbe-Schmitt synthesis. I. Role of the arylcarbonic salts in the mechanism of carboxylation. E. A. Shilov, I. V. Smirnov-Zamkov, and K. I. Matkovskii. Ukrain. Khim. Zhur. 21, 484-90(1955)(in Russian). The pressure of CO_2 from $PhOCO_2Na$ (I) at 170° is 6 atm. When C^{14}-labeled I or $2\text{-}C_{10}H_7OC^{14}O_2Na$ (II) is heated with unlabeled CO_2, the amt. of C^{14} in $o\text{-}NaO_2CC_6H_4OH$ and $2,1\text{-}HOC_{10}H_6CO_2Na$ formed is no more than would be present if the labeled C came through the gas phase. I and II are not intermediates in the reaction. John Howe Scott

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Inst. Org. Chem, AS USSR

SHILOV, Ye.A.; SMIRNOV-ZAMKOV, I.V.; MATKOVSKIY, K.I.

Theory of the Kolbe-schmitt synthesis. Part 2. Role of disubstituted salts in carboxylation. Ukr.khim.zhur. 21 no.5:600-613 '55. (MLRA 9:3)

1Institut organicheskoy khimii AN USSR.
(Carboxylation)

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USSR/ Chemistry - Organic chemistry

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Title : The form of the intermediate complex which resulted from regrouping of aromatic sulfo salts

Periodical : Dok. AN SSSR 100/4, 727-729, Feb 1, 1955

Abstract : Experiments were conducted with disodium salt of para-benzenedisulfonic acid and gamma-pyridine sodium sulfate to determine the form of the intermediate complex forming during the regrouping of aromatic sulfo acids. The results obtained are described. Five references: 2 USSR, 1 USA and 2 German (1899-1945).

Institution : Academy of Sciences, Ukr-SSR, Institute of Organic Chemistry

Submitted : August 2, 1954

SHILOV, Ye.A.; STREL'TSOVA, S.G.

Stereochemistry and the nascent-hydrogen reduction mechanism of multiple-bond compounds. Part 1. Reduction of tolan by metals in alcohols and acetic acid. Ukr.khim.zhur.22 no.3:341-346 '56.
(MIRA 9:9)

1.Institut otganicheskoy khimii AN USSR.
(Acetylene) (Reduction, Chemical)

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Chemistry as topic of the session of the Academy of Sciences of the Ukrainian S.S.R. devoted to the problem of peaceful use of atomic energy. Ukr.khim.zhur.22 no.3:409 '56. (MLRA 9:9)
(Radiochemistry)

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Stereochemistry and mechanism of reduction of compounds with multiple bonds by nascent hydrogen. II. Reduction of tolane by sodium in liquid ammonia. S. G. Strel'tsova and E. A. Shilov. *Ukrain. Khim. Zhur.* 22, 489-92(1956)(in Russian); cf. *C.A.* 51, 2007*e*.—$(PhC:)_2$ is reduced in liquid NH_3 to *trans*-$(PhCH:)_2$ and then to $(PhCH_2)_2$. *cis*-$(PhCH:)_2$ is isomerized under the conditions [illegible] the reduction and [illegible] be the initial product. [illegible] the authors [illegible] theoretical grounds. They visualize an addn. of Na to the triple bond followed by reaction with NH_3 and a 2nd Na atom to form $NaNH_2$ and *trans*-PhNaC:CHPh. Repetition of the process would form $(PhNaHC)_2$. The hydrocarbon products were recrystd. from alc. Et_2O has no effect on the reaction. Addn. of EtOH, $PhNH_2$, and *p*-$MeC_6H_4NH_2$ make the reaction much more rapid and no $(PhCH:)_2$ is isolated. If only half enough Na is used for total reduction, an equimolar mixt. of $(PhC:)_2$ and $(PhCH_2)_2$ is formed. John Howe Scott

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Inst Organic Chem, AS UkrSSR

Theory of nucleophilic addition. III. Kinetics of the addition of hydrogen bromide to dimethyl acetylenedicarboxylate from solutions of lithium bromide. V. G. Ostroverkhov and E. A. Shilov. *Ukrain. Khim. Zhur.* 22, 590-5(1956)(in Russian); cf. *C.A.* 50, 185*d*.—In the addn. of HBr to $(:CCO_2Me)_2$ (I) using an AcOH soln. of LiBr, $-d[HBr]/dt = k_2A[LiBr]$ [A = concn. of I, k_2 (moles/l. min.) = 5.88×10^{-4} at 30°, 1.49×10^{-3} at 40°, and 3.86×10^{-3} at 50°, E = 18.2 kcal./mole, ΔS^* = −18.9 cal./degree mole]. The rate does not alter much with addns. of H_2O, dioxane, or MeCN. If K_2' is the rate const. in the presence of H_2O, $K_2'/K_2 = 1.01-1.18\rho/D$, ($\rho$ = molar ratio of H_2O to LiBr in HOAc soln., D = dielectric const. of the mixt.). $PhC:CCO_2NH_2$ does not add HBr under these conditions.

John Howe Scott

Shilov, E. A.

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Stereochemistry and mechanism of reduction of compounds by nascent hydrogen. III. Reduction of acetylenic acids. S. G. Strel'tsova and E. A. Shilov. *Ukrain.* [illegible] 22, 596-602(1956)(in Russian); cf. *C.A.* 51, [illegible] The reduction of [illegible] PhC≡CCO₂H in 5M NaOH [illegible] pure Zn gives trans-PhCH:CHCO₂H (I). A 4:1 [illegible] couple gives 42% of PhCH:CHCO₂H (II) along with 52% I. This is the largest yield of II obtained. A Zn-Pt couple gives I, a 1:4 Zn-Ni couple forms 8% I and 18% II. The mechanism of the formation of I on pure Zn and II on combinations with Cu is discussed. J. H. S.

Chem

SHILOV E. A.

[illegible] I was [illegible] effective [illegible] ef-
some labeling [illegible] II. For-
fective. None is a direct pr[illegible]
mation of carotenoid pigments in the leaves of kok-saghyz
I. G. Vyval'ko, A. I. Dushechkin, G. M. Lushchevskaya,
and K. I. Matovskii. *Ibid.* 655–9.—HOAc-*1*-C^{14} increases
the amt. of labeled carotene in the leaves much more than
labeled levulinic acid, pyruvic acid-*2*-C^{14}, alanine, glycine,
glucose, or sucrose. The av. life of radioactive carotene in
the leaves is 3–5 days.

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