

3. D.D. Perrin. The stability of complexes of Ferric ion and Amino-acids // J. Chem. Soc. -1958. -P. 3125-3128.
4. D.D. Perrin. Stability constants of metals-ion complexes // Pt B: Organic ligands. Ed.D.D. Perrin. Oxford; New York; Toronto; Sydney; Paris; Frankfurt. Pergamon Press. -1979. -P.1263.
5. A. Iokovidis, N. Hadjiliadis. Complex compounds of platinum (II) and Iridium (IV) with amino acids, peptides and their derivatives // Coordination Chemistry Reviews. -1994. -№ 135-136. -P.17-63.
6. S L. Croft, R A. Neal, D. G. Craciunescu. The activity of platinum, iridium and rhodium drug complexes against *Leishmania donovani* // Journal Article, Research Support, Non-U.S. Gov't Trop Med Parasitol. -1992. Mar; -Vol. 43(1):-P. 24-8.
7. H T. Chifotides, N. Katsaros, G. Pneumatikakis. Complexes of azathioprine, a biologically active mercaptopurine derivative, with Pt(II), Pd(II), Rh(III), Ru(III) and Ag(I) // Journal of Inorganic Biochemistry. -1994. -V. 56. -Issue: 4,- P. 249-263.
8. M Z. Wiśniewski, J. Wietrzyk, A. Opolski. Novel Ru(III), Rh(III), Pd(II) and Pt(II) complexes with ligands incorporatingazole and pyrimidine rings. I. Antiproliferative activity in vitro // N Archivum Immunologiae et Therapiae Experimentalis. Institute of Chemistry, Pedagogical University, Checinska Poland. -2000. -Vol. 48, -Issue. 1, -P. 51-55.
9. K. Roland, P. Kurt, W. herbet, Z. Ingo, B. Wolfgang Metallkoomplex mitbiologisch wichtigen liganden, LIII chorale Halbsandwich-komplex von Rhodium(III), Iridium (III),Iridium (II) und Ruthenium (II) mit α -Aminosaeure-Anionen. // Chem.Ber. -1990. -V.123. -№.4. -P.767-778.
10. . A. Albert, E. Sergeant. The ionization constants of acids and bases. // -M. -1964. -C.10-33, 149-159.
11. N.N. Golovnev. New methods of the influence of pH on the equilibrium of complexation in aqueous solutions. // JI. -2000.-T.45.-№7.-P.1237-1240.
12. V.N. Alekseev. Quantitative analysis. M.: Chemistry. -1972. -C.329.
13. N.Y.Esina, M.N.Kurasova, W.M.Malaga, A.K.Molodkin, M.V.Tachaeve, V.E.Shapovalova, (2011), Complex formation of rodium (III) with hypoxanthine and adenine, Scientific and Technical Volga region Bulletin, Russia, №6, ISSN 2079-5920, 71 - 75.
14. K. Nakamoto. Infrared spectra of inorganic and coordination compounds.-M.: "World". -1966. -C.274.

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THE NEW ENVIRONMENTALLY PURE METHOD OF OBTAINING OF SATURATED CARBONIC ACIDS OF THE CONDITIONS INTERPHASE CATALYSIS

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SUMMARY

In the conditions of an interphase catalysis in the presence of crown-ether reactions of oxidation of primary alcohols, saturated hydrocarbons (C4 – C10) and saturated chlorhydrocarbons are investigated and easy, effective and new method for obtaining saturated organic acids is offered.

Use of crown-ether in the offered method allows to carry out process at low temperature and mild conditions, at the same time the same portions of crown-ether can be used many times without special cleaning and easily regenerated. The new simple technique is developed for cleaning and separation of crown-ether from reaction mixture after carrying out oxidation reaction. The reaction of oxidation of primary alcohols, saturated hydrocarbons (C4–C10) and saturated chlorhydrocarbons was carried out in two-phase heterogeneous system within 20-50 min. Quantity ratio of initial product: KMnO₄: DB18K6A, was 0.1: 0.3-0.4: 0.003-0.004. The process is smoothly carried out at 105^oC -160^oC temperature interval (against 450^oC -500^oC in usual conditions in the lack of the interphase catalyst) without formation of chlorine containing waste and also poisonous products.

The listed data provide the maximum yield of a target product.

The interphase catalysis is one of the most interesting, perspective and developing fields of synthetic organic chemistry.

Discovery of a new method of an interphase catalysis for rather short time was generally recognized and also the widest application in all fields of organic chemistry as one of the universal methods of synthesis. IFC was taken advantage at once and took an important place in organic synthesis, having forced out many old ways. It rendered powerful impact on development of new, convenient technological ways in industrial scale [1-6].

The known ways of receiving saturated carbonic acids are based on process of oxidation of saturated hydrocarbons (C4 – C10) in steam phases at a temperature of 450-5000C and 150-200 atm. pressure and oxidation of aliphatic alcohols with aqueous KMnO₄ solution, and also oxidation of saturated halogenalkans [7-9]. However these ways have a number of shortcomings, of which the following is essential: 1) high temperature up to 500^oC, 2) an isomerization and an molding of the reaction product under the high temperature, 3) use of rather big excess (more than 100%) of potassium permanganate, 4) obtaining of thousands tone of chlorine-containing waste, and also poisonous

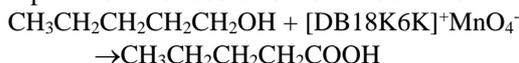
CO, CO₂, Cl₂ and HCl vapours which are thrown out the environment and pollute the atmosphere, 5) a low yield of a target product, 6) owing to the listed reasons hopelessness of industrial realization is revealed.

The listed disadvantages required development of a number of new ecologically efficient methods. With this purpose we carried out reactions of oxidation of saturated hydrocarbons (C₄ – C₁₀), alcohols and also the saturated halogenalkans in the conditions of an interphase catalysis (IFC) with application of crown-ethers.

Establishment of the main regularities of a reaction of oxidation of primary alcohols, saturated hydrocarbons (C₄ – C₁₀) and saturated halogenalkans in the conditions of an interphase catalysis, establishment of a role of the major factors defining the reaction proceeding in liquid – solid phase system and development of a new, convenient, environmentally pure way of obtaining of saturated organic acids in mild conditions with high yields are the goals of the given research.

The reaction of oxidation of initial products was carried out in two-phase heterogeneous system consisting of solid salt of KMnO₄, an initial product in the presence of the interphase catalyst in organic solvents.

N-pentanol was chosen as model connection.



The proceeding of oxidation reaction of primary alcohols at a catalysis by crown-ethers is characterized by existence in system of macrocyclic ether which plays the role of transformer of permanganate ion (MnO₄⁻) from a solid phase to organic solvent. Essence of a catalysis is that DB18K6 transfers permanganate ion to an organic phase by a complex formation and thereby, promotes its dissolution.



In this phase the complex, dissociating, represents extremely active permanganate ion which reacts with primary alcohols and oxidizes it to saturated organic acids

Reaction rate in the applied system depends on a number of factors. The nature of a solvent, crown-ethers, concentration of KMnO₄ and crown-ethers, and also availability of water in the system are the most essential. As the interphase catalysts (IC): crown-ethers -dibenzo-18- crown-6 (DB18K6), 18- crown-6 (18K6), pentamethyl-15- crown-5 (PM15K5), tetramethyl-12- crown-4 (TM12K4), and also widely applied quarternary ammonium salt – triethylbenzylammoniumchlorine (TEBA) were used. Besides for comparison reactions were also carried out without interphase catalyst.

As solvent toluene, xylol, 1,4 dioxane, diglym, n-butanol, ethylene glycol were used. The reaction was also carried out without solvent. Reaction temperatures were 105°C, 130°C, 170°C.

Studying of the influence of the solvent nature on an yield of pentane acid showed that the maximum yield of pentane acid is observed in the lack of solvents due to the best solubility of DB18K6 and its complex with KMnO₄ in hydrocarbons and in the case

getting of high concentration of reagents and the catalyst.

When carrying out reaction in various solvents in the systems liquid - solid phase it was established that aprotone cation solvating solvents are preferable hydrocarbonic solvents then– first of all aromatic ones.

The greatest yield of pentane acid is reached in a diglym (98%).

Yield of pentane acid depending on the applied solvent decreases in the following order:

without solvent > diglym > dioxane > ethylene glycol > xylol

Influence of the nature crown-ethers on an yield of pentane acid is studied too.

It is established that the used crown-ethers on activity are placed as follow:



The maximum yield of pentane acid is observed in application of DB18K6 and 18K6 due to the best complexforming ability of those crown-ethers with KMnO₄.

Gradual decrease of cavity sizes of crown-ether upon passing from 18K6 to PM15K5 and to TM12K4 leads further to reduce of pentane acid yield. Without crown-ether formation of pentane acid is not observed. An yield of pentane acid is also influenced by change of DB 18K6 and KMnO₄ concentration.

Increase in concentration of KMnO₄ from 0,1 to 0,5 mol increases an yield of a target product. However, increase in concentration of KMnO₄ more than 0,5 mol causes collateral processes.

Similar to increase in quantity of DB18K6 from 0,001 to 0,005 mol leads to gradual increase of an yield of pentane acid. The maximum yield is reached at application of 0,004 mol of DB18K6 concentration.

On the basis of the analysis of all experimental data it was succeeded to develop rather easy technological way of obtaining saturated carbonic acids with high yield. For experimental application DB18K6 or 18K6 KMnO₄ -systems in aromatic hydrocarbons or in simple ethers were offered.

In rather pure look and developments of the way accepted for receiving a wide number of carbonic acids it is required to apply several modified options of implementation of oxidation to an exception of collateral reactions, a possibility of allocation of a target product. On one of them, an initial product, crown-ether and KMnO₄ in solvent or without solvent are mixed at 105°C-170°C before full transformation of initial compound, and then reaction mixture is subjected to processing to full transformation of initial compound (option A). The option A is convenient for obtaining of easily boiling (to 175°C) saturated carbonic acids.

Option A. Place 0.3-0.4 mole KMnO₄ powder into the reaction vessel supplied with an effective mixer, distillation cup, the descending refrigerator and a drop funnel, add KMnO₄ powder into the high-boiling solvent, 0.003-0.004 mole crown-ether, turn on a mixer and heat reaction mixture. Temperature is to be and more than 20°C higher than the boiling product. At achievement of this temperature from a drop funnel slowly alcohols or halogenalkans are add-

ed. The product distillation begins soon. After adding of all initial product, heating and a mixing of reaction mixture continue till a product distillation stop.

Processing. The product is dried over carbonic potassium and subjected to repeated distillation. In a reactionary vessel there is a solution of the taken crown-ether in some polluted solvent at the bottom of which there is a dropped-out MnO_2 deposit. Solution of a crown-ether in a hot form is separated by decantation. This solution is suitable for carrying out repeated analogical experiences, without use of additional quantity of crown-ether and solvent and at the same time the catalytic effect of crown-ether does not worsen at all. Thus, in the offered way the expense of the most expensive component of reaction- crown-ether does not occur and even solvent is not lost.

Advantage of this way known in comparison with known ones consists in the following:

- 1) There are no collateral processes - isomerization and molding;
- 2) The way is simple in implementation and there is an opportunity for continuous conducting process;
- 3) Crown-ethers and solvents are not spent, and the same quantity is used. Only periodic regeneration is required that is easily feasible;
- 4) There is no processing stage of reaction mixture with the purpose of separation of a product.

It is undoubted that all these makes the method simpler and profitable.

Option B. Place $KMnO_4$ powder into a reaction vessel, add crown-ether, an initial product (the ratio of reagents and crown-ether is the same, as in option A), add easily boiling solvent and reaction mixture at vigorous mixing and boil with the descending refrigerator. Reaction time depending on reaction ability of initial compound, concentration of crown-ether and $KMnO_4$, and also from the temperature, varies from 20 min. to 60 min. It is possible to watch the proceeding of reaction by gas liquid – chromatografio method and the tests which are selected on time from reaction mixture.

Processing. At the end of process reaction mixture in the hot form is separated from the dropped-out deposit and cooled, filtering via the paper or glass filter with crown-ether isolation, and further a filtrate distillation.

The solvents and crown-ether after such experiments are also suitable for the subsequent similar experiences after drying, but without additional special cleaning.

Option A in comparison with option B has undoubted advantage that because of the low temperature of carrying out reaction, passing of collateral processes of an molding, isomerization, etc. is completely excluded. The top limit of temperature in this case makes 140° .

Regeneration of crown-ether and solvents

In case of need the solvents are regenerated by simple distillation, and crown ether- by transmission of their solutions through a column with silicagel and with the subsequent concentration of solution. Crown-ether which dropped out of such solutions separates by filtering as it is described above. Instead of a column with silicagel it is also possible to use a column with an oxide of aluminum or the way, offered in work [10].

Reaction rate in the offered system can be changed in the wide range, varying:

- a) the quantity of crown ethers- the more quantity of crown ether with other things being equal, the higher reaction rate,
- b) the quantity of $KMnO_4$ - the bigger surplus of $KMnO_4$, the higher reaction rate. But from bigger surplus of $KMnO_4$ molding danger occurs,
- c) experiment temperature,
- d) moisture content in $KMnO_4$ or solvents – the higher moisture content in system, the rate of reaction is lower and because of $KMnO_4$ moisture from strong aggregate state passes into liquid, then reaction rate sharply falls. Therefore an indispensable condition of successful carrying out of reaction is existence of $KMnO_4$ in a solid state.

When developing the method as reagent of phase transfer two crown-ethers are used-dibenzo-18- crown -6 (DBK18K6) both 18- crown -6 (18K6) and one widespread reagent of phase transfer- quarternary amine-triethylbenzilammoniumchloride (TEBA).

As the high-boiling solvents depending on temperature of boiling of the obtained acids diethyl benzene (ESD), cumene (QOM) and other aromatic or alkylaromatic hydrocarbons and simple ether can be used.

As the low-boiling solvents benzene, toluene, mixture of isomeric xylols, dioxane, etc. can be used.

The received optimum results are reflected in table 1.

Table 1. Oxidation of halogenalkans and limit alcohols (0.1 mole initial product, 0.3 mole KMnO_4 , 0.003 mole of crown-ether, 10 ml solvent)

Number reaction	Initial product	Option reactions	Reaction conditions	Reaction product	% yield
1.	Butanol-1	A	DB18K6, 105°C, 50 min.	Butane acid	98
2.	Pentanol-1	A	DB18K6, 135°C, 50 min., xylol	Pentane acid	95
3.	Hexanol-1	B	DB18K6, 160°C, 30 min. tetragly	Hexane acid	96
4.	Heptanol-1	B	DB18K6, 160°C, 40 min.	Heptanoic acid	96
5.	Octanol-1	B	DB18K6, 170°C, 20 min.	Octane acid	95
6.	Chlorpentane-1	A	18K6, 140°C, 30 min., xylol	Chlorpentane acid	92
7.	Brompentane-1	A	18K6, 140°C, 30 min., diglyme	Brompentane acid	93
8.	Chlorhexane-1	A	18K6, 140°C, 30 min., diglyme	Chlorhexane acid	95
9.	Bromhexane-1	A	18K6, 101°C, 30 min., dioxane	Bromhexane acid	96
10.	Chlorheptan-1	B	DB18K6, 140°C, 40 min., diglyme	Chlorheptanoic acid	93
11.	Bromheptan-1	B	DB18K6, 140°C, 40 min., diglyme	Bromheptane acid	96

For the option A temperature of reaction mixture is specified, for option B- temperature of oil bath.

From the table 1 it is seen that not only alcohols are successfully turned to carbonic acids but also halogencontaining saturated alkanes. And successful transformation occurs not only with use of bromides, but also less reactive chlorine-containing saturated alkanes.

EXPERIMENTAL PART

Purity and identity of products were determined by method of a gas-liquid chromatography, and also as a result of definition of physical constants. Analyses were carried out on the LHM-8MD device (model 3A) with the flame and ionization detector. The column of 1.5 m long with 3 mm internal diameter was filled with chromatom N-AW-DMCS fraction by 0.20-0.25 mm with the silicone SKTFT-50 rubber (5% of the mass of the carrier) applied on it.

Obtaining of pentane acid (option A with solvent, see reaction table 2). 8.8 g (0.1 mole) pentanol-1, 1.2 g (0.003 mole) DB18K6 was placed into reaction, flask 10 ml of xylol was added and when mixing in one step 47.4 g (0.3 mole) KMnO_4 was added. Reaction mixture while mixing was boiled 50 min. Upon the end of reaction the organic phase in hot form was separated from the dropped-out sediment by decantation. The remain was extracted by 5 ml of hot xylol. When cooling from the integrated organic phase DB18K6 was recrystallized and separated by filtering via the glass filter. The filtrate was subjected to distillation under the reduced pressure.

Yield 9.7 g (95%); t_{boil} . 60 °C /5 mm; n D20 1.3955.

Literary data [11]: t_{boil} . 187 °C, n D20 1.3952.

Obtaining of chlorpentane acid (option A without solvent, see table 1 reaction 6). 10.6 g (0.1 mol) to chlorpentane-1, 1.2 g (0.0042 mol) 18K6, were placed into reaction flask when mixing in one step 47.4 g (0.3 mol) of KMnO_4 is brought. Reaction mixture was heated on an oil bath to 150 °C within 30-40 min. For this period KMnO_4 is released from MnO_2 particles, the reaction mixture was periodically mixed by mechanical mixer. Upon the end reaction mixture was extracted 5 ml of hot toluene, and the integrated extracts were subjected to distillation. In this case used crown-ether remains in the form of oil at the bottom of a distillation flask.

Yield 12,6 g (92%), t_{boil} . 107,8 °C, nD20 = 1,4127, d = 0,8818.

Literary data [12]: t_{boil} . 107,8 °C, nD20 = 1,4127, d = 0,8818.

Obtaining of hexane acid (option B with solvent, see table 1, reaction 3). 10.2 g (0.1 mole) hexanol-1 and 1.2 g (0.003 mole) DB18K6 were placed into reaction flask with descending refrigerator, mixing in one step 31.6 g (0.2 mole) of KMnO_4 and 10 ml of a tetraglyme. At constant mixing the temperature of an oil bath was slowly increased to 160 °C and hexane acid was obtained.

At the decrease of distillation rate bath temperature was slowly raised to 165 °C, and at the end of reaction for a short time – to 170 °C. The product obtained, except water, did not contain any impurity.

Yield 11.1 g (96%), t_{boil} . 72°C/ of 5 mm, nD20 = 1,4147.

Literary data [11]: t_{boil} . 205°C, nD20 = 1,4150.

References

- Hiraoka M. Crown compounds. M, World. page 212. 1986.
- V.'s Weber, Gokel G., Interphase catalysis in organic synthesis. M, World., 1980.
- Pedersen C.J., J.Am. chem Sos. 89(26)7017 (1967)
- Verzhichinskaya S. V., Tees A.D., Oshchepkov M. C. Crown-ethers, as catalysts - of mercaptan oxidation. Achievements in chemistry and chemical technology. Volume XXVII.2013.№4.стр.34-38.
- Guseynova T. M. Study of regularities of dehydrohalogenation of - 1,2-dihalogenethylbenzol in the conditions of an interphase catalysis. XI All-Russian scientific and technical conference Moscow "Urgent Problems of Development of an Oil and Gas Complex of Russia". 2016 p. 211.
- Guseynova T. M. Oxidation of aniline at the presence of crown ether. "Materials XXVII International scientific and practical conference " Moscow. 2016 p. 61-63.
- Tittsa L., Aykher T., Preparative organic chemistry, "Mir" Moscow, 2009, page 140
- Knight D.W. Gen.Synth. Methods, 10, 75 (1988).
- Rock J., Ng C.S. J. Organic Chemistry, 38, 3348 (1973).
- Guseynova T. M. Cleaning of crown-ether. Azerbaijan Chemistry Journal, No. 2, Baku, 1984, page 39-41.
- The practicum on organic chemistry / Costa A. N. M.World, 1965, page 412.
- Properties of organic compounds / the Reference book. Potekhin.-1984.-page 26