

SCF-ISOPROPANOL AS A REAGENT IN ORGANIC, ORGANOMETALLIC AND INORGANIC CHEMISTRY.

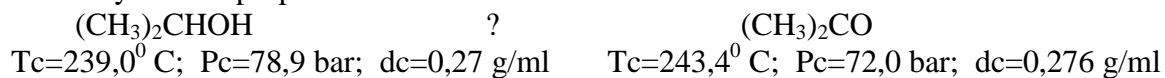
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INTRODUCTION

It is well known, that properties of SCFs are different from those of ordinary liquids and gases. When we say properties we usually mean density, viscosity, solubility, solvating power and so on, which change dramatically at the conditions close to the critical point. But not so much is known about the change of chemical reactivity at the transition from subcritical into supercritical state.

The system isopropanol-aceton:



is unique from supercritical point of view: the main parameters of these compounds are nearly the same. Probably the agreement of these parameters of the two substances in supercritical state is the cause of the easiness with which SCF-isopropanol give its two hydrogens to various substrates.

We used this property and showed, that SCF-isopropanol could be wonderful reagent-reducing agent (donor of two hydrogens) in organic, organometallic and inorganic chemistry. We discovered this property more than 20 years ago; it has been shown in our old publications that the treatment of dry coal with alcohols under supercritical conditions led to the formation of considerable amounts of liquid product, which was significantly enriched with hydrogen in comparison with the hydrogen contents in the organic part of the initial coal [1]. The corresponding amounts of carbonyl products of alcohol dehydrogenation are found among light fractions. These experiments became the basis of the development of the technology of brown coal destructive hydrogenation to produce the constitute of the oil mazut with unique low content of sulfur (lower than 0,1%). And then experiments with model compounds have shown [2], that hydrogenation (and alkylation) by SCF-alcohols of organic compounds with multiple bonds under supercritical conditions occurred without catalysts [3]. The alcohols differ on their reactivity in relation to the same substratum very strongly and place on hydrogenating capacity in the following order: $(\text{CH}_3)_2\text{CHOH} \gg \text{C}_2\text{H}_5\text{OH} > \text{CH}_3\text{OH}$ [4]. At the same time the alkylating capacity increases in the reverse direction. It is well known, that in subcritical conditions the alcohols

without catalysts have no hydrogenating capacity.

Study of reactions of various types of organic, inorganic and organometallic compounds with isopropanol has been conducted as in the field of subcritical, and also supercritical one of alcohol. In this paper, we generalize the results of our investigations, which roughly revealed the applicability limits of the method and its potentialities.

MATERIALS AND METHODS

Chemicals. All commercial chemicals were reagent grade.

Instrumentation. For performance of experiments at high pressures we designed two versions of autoclave techniques: by welded ampoules (for organic, organometallic compounds and oxides) and opened glass containers (for the reactions of SCF-isopropanol with the oxides). The transition in the supercritical state has been conducted by temperature rise of the reactor and accordingly internal pressures. The standard experiments have been performed at temperatures and pressures, which significantly (on 50-70⁰ C and more) exceeded than critical ones of isopropanol to leave from area of instability, which usually occurred in the field of phase transition. After cooling and discovery of ampoules (in case of an ampoule method), the solid phases was studied by X-ray analysis, DTA, TGA and the liquid ones – by GC and GC-MS. X-ray analysis has been conducted on a diffractometer Geigerflex, Cu Ka - radiation, Ni - the filter. Differential thermal (DT) and thermogravimetric (TG) analyses have been executed on STA- 409 Netzsch thermoanalyser on air in crucibles from platinum or Al₂O₃. Heating and cooling velocity was 5 grad / min.

RESULTS

ORGANIC COMPOUNDS

Compounds with multiple bonds were first studied. SCF-isopropanol was found to hydrogenate anthracene to 9,10-dihydroanthracene with the yield higher than 80%. The double bond of styrene exhibits the same activity in this reaction, which always additionally yields small amounts of polymerization products (a mixture of oligomers). Unsaturated aliphatic compounds were less active: under the same conditions, 1-hexene was hydrogenated only by 50%:

anthracene ? 9,10-dihydroanthracene (80%),
C₆H₅CH=CH₂ ? C₆H₅CH₂CH₃ (80% + polymer),
CH₂=CH-(CH₃)₃-CH₃ ? CH₃(CH₂)₄CH₃ (50%).

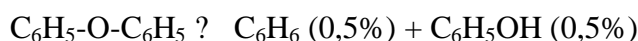
In all the cases, the second product of the reaction is acetone, whose amount corresponds to the amount of hydrogenation product. A specific feature of the process is that, in spite of high temperatures of the reaction (~400°C), it never resulted in the products of decomposition, carbonization, resinification, etc.: after completion of the reaction, the resulting mixture was always a transparent solution of the reaction products in alcohol.

In addition to hydrogenation of multiple bonds, hydrogenolysis of ordinary carbon-carbon bonds of the *sp*³-*sp*² and *sp*³-*sp*³ types is possible:

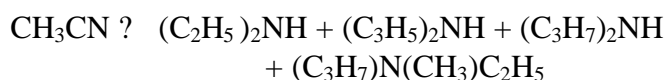
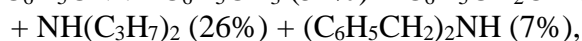
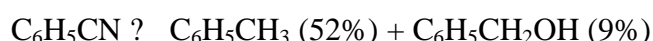
C₆H₅-CH₂-CH₂-C₆H₅? C₆H₅CH₃ (20%) + C₆H₅CH₂CH₃ (1,5%)
C₆H₅-CH₂-C₆H₅? C₆H₆ (1,5%) + C₆H₅CH₃ (1,5%)

1,2-Diphenylethane produces toluene and ethylbenzene in amounts, which are inversely

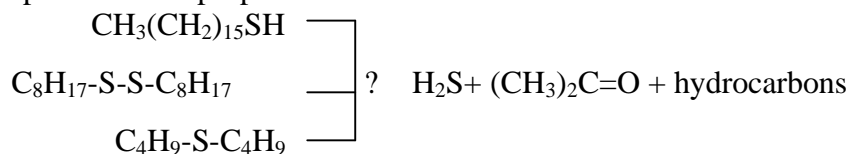
proportional to the strengths of the corresponding bonds; diphenyl-methane is naturally much less active in this reaction. A similar situation was also observed in the case of heteroelement bonds. Multiple bonds are hydrogenated, and ordinary bonds are hydrogenolyzed:



Multiple C=O bonds are seen to be as active in this reaction as C=C bonds. As one would expect, the bonds in diphenyl ether are much less reactive than similar bonds in dibenzyl ether. The main product (with the yield higher than 80%) of nitrobenzene hydrogenation is aniline, which is partially alkylated under the severe experimental conditions:



Whereas hydrogenolysis upon benzonitrile reduction proceeds virtually by 50%, toluene forms in amounts comparable to the total amount of nitrogen-containing products. By the example of acetonitrile, the results of transalkylation of the initially formed ethylamine are clearly seen. C-S bonds, which are more active in hydrogenolysis, are easily ruptured by supercritical isopropanol:



Under the conditions of the reaction, mercaptans, sulfides, and disulfides, including those with the least active long hydrocarbon radicals, were virtually quantitatively desulfurized. Under these conditions, dibenzothiophene modeling the least active part of organosulfuric compounds of heavy oil fractions is only partially desulfurized (by 35%). Alcohols dramatically differ in their ability to hydrogenate the same substrate.

Isopropanol is most active in hydrogenation, whereas methanol is most active in alkylation. It is characteristic that tert-butanol having no α -hydrogen and diethyl ether having no OH groups cannot hydrogenate or alkylate the same typical substrates, specifically, anthracene and phenol. Thus, for the reaction to proceed successfully, the molecules of supercritical fluid should necessarily have both OH groups and α -hydrogen. The reactions occur well at a solvent: the substrate ratio higher than 100:1. The driving force for the reaction is probably the clustering of a large number of molecules of supercritical fluid around a substrate molecule: solvent molecules in such a cluster are considered [5].

to collapse so that the local density of a supercritical fluid in a cluster is much higher than the density of the corresponding liquid. It is probably the fact that makes the migration of two hydrogen atoms from an alcohol molecule to a substrate molecule energetically allowed.

ORGANOMETALLIC COMPOUNDS

In the light of mentioned above “purity” of the high-temperature reactions in SCF-isopropanol it was natural to pay attention at the organometallic compounds. Many of them are labile at thermal reactions.

Ferrocene and other organometallic p-complexes are stable enough to catalytic reduction by hydrogen [6]. We found the SCF-isopropanol reacted with ferrocene with the formation of metallic Fe and cyclopentane. The reactivity with the methanol is more interesting. It is known, that ferrocene is very active in the reaction of aromatic substitution. We have found, that ferrocene, as well as phenol, were methylated easily by SCF-methanol. The mixture of mono- and dimethylferrocene was obtained as the result of this reaction. More interesting result was obtained at the interaction of tolylenechromiumtrycarbonyl with SCF-methanol. The main product of the reaction was the mixture of the xylenes. Non-coordinated toluene was not alkylated by SCF-methanol under these conditions. Probably the coordinated toluene was methylated but the forming xylenechromiumtrycarbonyls were less stable in the conditions of the reaction and decomposed with the formation of the free xylenes. The interaction of SCF-alcohols with $\text{CpMn}(\text{CO})_3$ and with bis-arenechromium have been studied also.

INORGANIC COMPOUNDS

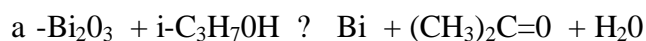
Similar reactions are also possible when substrate is a completely alcohol-insoluble solid substance. Inorganic substrates, specifically, metal oxides, sulfides, and halides can also react with SCF-isopropanol under these conditions. Binary and mixed metal oxides form a vast class of inorganic compounds. Their unique physical characteristics (magnetic, optical, electrical, and others) stimulated researchers to study their structure and reactivity. Among the numerous problems existing in this field of chemical materials science, the following are the most attractive:

- (1) the development of synthetic methods for suboxides, their structural characterization, and the production of cluster structures;
- (2) fine control over oxygen stoichiometry in phases of variable composition;
- (3) control over the composition and structure of near-surface layers of mixed oxide single crystals;
- (4) the intercalation of an oxide host with organic compounds, hydrogen, and other reactants;
- (5) controlled reduction of mixed oxides targeted at preparing compounds with a desired ratio of *d* elements with various oxidation numbers; and so on.

We believe that the aforementioned unique properties of SCF alcohols are applied to approach some problems from the above list.

The interaction of the oxides of different elements of I-VII groups with SCF isopropanol has been studied as in subcritical and also in supercritical areas. The oxides of transition and non-transition elements have been used for the research. At first we studied the heterogeneous reaction of metal oxide and SCF-isopropanol on the example of a $-\text{Bi}_2\text{O}_3$ as representative quoter of oxides of nontransition elements.

We have found, that the interaction of a $-\text{Bi}_2\text{O}_3$ with i-PrOH above critical point of alcohol (235°C) proceeded as following:



The analysis of a fluid phase has shown that alongside with initial isopropanol acetone was

present in it in stoichiometric amounts. The realization of experiment in the special installation, permitting visually watch the reaction, has shown, that the achievement of critical temperature for isopropanol was accompanied by disappearance of a meniscus; during the whole reaction any phase separation in a system was absent. Thus the solid phase at the bottom ampoules was saved during all time of experiment, only changing the color and form.

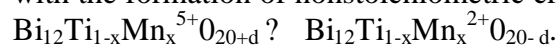
By this means, the found reaction represents solid-phase reduction of bismuth oxide up to bismuth-metal under SCF-isopropanol [7].

Different oxides of the elements of I-VIII system have been tried in the reaction of SCF – isopropanol. They can be divided into 3 groups on their reactivity:

- 1) oxides, that were reduced up to metal (CuO, CdO, PbO, Sb₂O₃, Bi₂O₃, Co₂O₃, ReO₃, PtO₂);
- 2) oxides of metal with the variable valences, which were reduced up to low oxidation levels (V₂O₅, Fe₂O₃, MnO₂, Mn₂O₃, MoO₃)
- 3) oxides, that were not reduced by SCF-isopropanol at all (UO₂, , WO₃, ZrO₂, CeO₂, SiO₂, GeO₂).

The interaction of the rare element oxides Ln₂O₃ (Ln=La, Nd, Sm, Eu, Gd, Dy, Yb) and CeO₂ with SCF-isopropanol has been studied. The reaction of hydrogenation of the oxides (except CeO₂) with the formation of corresponding hydroxides has been found.

The possibility of the “extraction” of oxygen from the surface of series of complex oxides with the formation of nonstoichiometric crystalline oxides has been shown; for example:



The interaction of monocrystal Bi₁₂Ti_{1-x}Mn_xO₂₀ with *i*-PrOH above critical temperature demonstrated the possibility of selected “withdrawal” of oxygen from crystal lattice of phase with the sillenite structure. The initial monocrystal Bi₁₂Ti_{1-x}Mn_xO₂₀ had green color because of presence Mn⁵⁺ and Mn⁴⁺.

When the oxygen stoichiometry of the crystal Bi₁₂Ti_{1-x}Mn_xO₂₀ changed (for example at annealing in vacuum) [8] the decrease of degree of Mn cations oxidation took place up to +2 (Mn⁵⁺ and Mn⁴⁺ → Mn²⁺). As Mn²⁺ had no bands of absorption in the visible field of spectra, the color of crystal changed from green on yellow (the usual color of unalloyed crystals Bi₁₂TiO₂₀).

The conditions of SCF extraction of oxygen from the surface of monocrystals of oxydes Bi₁₂MO₂₀ (M = Si, Ge, Ti) in the depth up to 1.5 mm with the simultaneous modification (decrease) of the valences of cations M have been found. The interaction of the crystals Bi₁₂TiO₂₀ (BTO) <Cu>, BTO<Mn> and BTO<Cr> with SCF has been accompanied by the change of the charge of alloying impurities: Cu⁺² → Cu⁺, Mn⁺⁵ → Mn⁺² and Cr⁺⁵ → Cr⁺⁴, that led to the corresponding changes in absorption spectra, in the circular dichroism and photoinductional absorption spectra. The change of charge of alloying impurity was absent in the crystals alloyed by N and V. The method of the treatment of crystals by SCF *i*-PrOH permits the selective oxygen extraction from the volume of the crystals.

CONCLUSION

The numerous examples of the reaction presented here demonstrate that the unique reactivity of SCF-isopropanol just above the critical point can be applied beneficially in various ways in organic, organometallic and inorganic chemistry.

There is a broad range of chemical transformations that can be effected in the nonconventional reaction medium of supercritical isopropanol. These transformations include

hydrogenation of different types of bond, hydrogenolysis, hydrodesulfuration, hydrodehalogenation. The rates and selectivities of these different reactions can be manipulated by the judicious selection of temperature, time of reaction and concentration. Although many fundamental aspects have not been clarified, the potential of SCF-isopropanol as a reagent in chemistry is already substantial, as the various examples shown in this communication demonstrate.

REFERENCES

- [1] GUBIN, S., KIRILEZ, V., MEN'SHOV, V., RIJKOV, E., PLOPSKY, E., Dokl. Akad. Nauk SSSR, Vol. 268, **1983**, p.1129
- [2] GUBIN, S., KIRILEZ, V., MEN'SHOV, V., Izv. Akad. Nauk SSSR, Ser.Khim., N 12, **1983**, p. 2835
- [3] GUBIN, S., KIRILEZ, V., MEN'SHOV, V., Izv. Akad. Nauk SSSR, Ser.Khim., N 9, **1985**, p. 2159
- [4] GUBIN, S., Dokl. Akad. Nauk SSSR, V.345, **1995**, p. 490
- [5] BETTS, T., ZAGROBELNY, J., Bright, F., J. Am. Chem. Soc., 1992, Vol. 114, N 21, p.8163.
- [6] Methods of organoelement compounds. Organoiron compounds. Ferrocene. Edited by NESMEYANOV, A., KOCHESHKOV, K., M.: Nauka, **1983**, 544p.
- [7] BUSLAEVA, E., KRAVCHUK, K., KARGIN, Yu., GUBIN, S., Inorganic materials, Vol.38, N6, **2002**, p.706
- [8] BURKOV, V., EGORICHEVA, A., KARGIN, Yu., VOLKOV, V., Inorganic materials Vol. 32, **1996**, p.860