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Oxidative Functionalisation of Cyclanes in the Presence of Transition Metal Salts

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Abstract

The data on liquid-phase oxidation of methyl- and ethylcyclohexanes by air oxygen in the presence of transition metals (Co, Cr, and Ni) naphthenates are presented. Their physicochemical, thermogravimetric, and spectral characteristics are examined. The introduction of cobalt naphthenate into the system leads to a significant drop in the yield of naphthenic acids, but the content of oxyacids increases significantly (more than 30 %), as established. To achieve the maximum yield of naphthenic acids, the optimum content of chromium naphthenate is 0.2 mass %, while that of oxy-naphthenic acids, cobalt naphthenate concentration is 0.3 mass %.

Keywords: cyclane, methylcyclohexane, ethylcyclohexane, transition metals, liquid-phase oxidation, naphthenic acids, oxy-naphthenic acids

INTRODUCTION

The processes of oxidation of hydrocarbons are most promising during the preparation of valuable and quite reactive hydroperoxides, oxides, ketones, lactones, acids, and alcohols that are important intermediates in industrial organic synthesis.

Among oxidation reactions, processes of liquid-phase oxidation of cyclane hydrocarbons with the prevailing formation of acids are of a special importance. Naphthenic acids (NA) are present in limited quantities (1.5–2 %) in naphthenic base oils, however, the range of their use is quite wide. A large number of the generated oxygen compounds make the process of oxidation of cyclanes ineffective and various catalysts and oxidising agents are used to increase process selectivity.

The use of transition metals compounds forming intermediate complexes between metal compounds and molecules of reagents allows directing the process to the way providing the formation of a desired product. The character of oxidation depends substantially on the cyclane structure and the presence of alkyl radicals that initiate a chain oxidation reaction. The process of oxidation of cyclanes is very similar to that of paraffinic hydrocarbons. However, the presence and the size of cycles substantially affect the progression of the process and the formation of target products. The use of transition metal naphthenates in oxidation processes of naphthenic hydrocarbons also used in the preparation of synthetic fatty acids has a number of significant advantages and allows substantially increasing reaction rates and contributes to industrial implementation of preparation process of synthetic NA [1, 2]. A large number of metal complexes that are able to activate a C–H bond in cycloalkanes have been detected [3–5]. It is much more difficult to expose cycloalkane species to functionalization in other words, to replace a hydrogen atom for a functional group (–OH, –COOH, Hal, *etc*.). The most accessible and efficient procedure for oxidative functionalization of cycloalkanes is their oxygen oxidation. To date several industrial processes of oxidative functionalization of saturated hydrocarbons are known, in particular the process of oxidation of cyclohexane to cyclohexanol and cyclohexanone and then to adipic acid [6]. The use of some compounds of Ru and V (heteropolytungstates) substantially increases the rates of decomposition of hydroperoxides and increases process selectivity. The oxidation of cycloalkanes in the presence of Ir and Pd complexes proceeds *via* different mechanisms. The Ir complex increases the efficiency of cyclohexane oxidation by *m*-chloroperoxybenzoic acid in 3 times. The use of Pd complexes for the oxidation of cyclooctane by hydrogen peroxide results in the formation of one product – cyclooctylhydroxyperoxide without participation of free hydroxyl radicals [7–9]. The presence of alkyl substituents in cycloparaffin species largely initiates oxidation reactions. The right selection of catalysts and reaction conditions allows directing the process *via* the route of transferring an oxygen atom, *i.e.* by a molecular mechanism, and carrying out oxidation with preserving the configuration of cycloalkanes. The functionalization of cycloalkanes proceeds *via* the formation of the bond $\text{R-Me}^{n+}\text{X}$. At the introduction of an oxidant into the system the active centre transforms into the complex $\text{R-Me}^{(n+2)}\text{X}_3$, in which the metal is presents in an oxidised state:

$\text{R-Me}^{(n+2)}\text{X}_3 \rightarrow \text{Me}^{n+}\text{X}_2 + \text{RX}$

X = OH–, COO–, Cl–

In accordance with another mechanism it is possible to use catalytic systems wherein one component (A) is responsible for the activation of a cycloalkane molecule, and another (B) for oxygen activation:

$\text{A}^{n+}\text{X}_2 + \text{RH} \rightarrow \text{RA}^{n+}\text{X} + \text{HX}$

$2\text{B}^{m+}\text{X} + \text{O}_2 \rightarrow \text{B}^{(m-1)+}(\text{OOH})\text{X} + \text{B}^{(m-1)+}\text{X}_2$

At present it is established that that among hydrocarbons, the process of oxidation of aromatic hydrocarbons and primary C–H bonds in paraffins occurs most difficultly [10, 11]. Alkylaromatic hydrocarbons and olefins undergo oxidation significantly easier, while cycloalkanes are mainly oxidized as alkanes.

EXPERIMENTAL

Leaching of technical NA with a 10 % NaOH solution was performed during Cr, Co, and Ni naphthenates preparation in the first step. The reaction was carried out in a three-neck flask with constant stirring at 70 °C for 2 h. The second step of synthesis was the preparation of metal naphthenates. This reaction is an exchange process between sodium naphthenate and metal salts (CoCl_2, NiCl_2, and $\text{Cr(CH}_3\text{COO)}_3$). Kerosene was added into the reaction mixture as a solvent, as metal naphthenates were water-insoluble. The reaction lasted 4 h at 70 °C with constant stirring. After rinsing, dewatering, and drying the product, the yields of naphthenates were 80–86 %. The structure of the resulting naphthenates was examined using spectral analysis methods (UV and IR). Infrared spectra were taken using a UR-20 device in a thin layer at 4000–700 cm^{-1} frequency range, cuvettes with lids made of NaCl, 1.26 mm thickness. Ultraviolet spectra were recorded using a JENWAY 6850 UV/VIS device, quartz plates with a thickness of 1 cm.

Samples of the synthesized catalysts were also exposed to derivatographical analysis of the thermal stability using a Q-1500D device. The analysis was conducted in air atmosphere, heating is up to 1000 °C, 200 mg suspension,

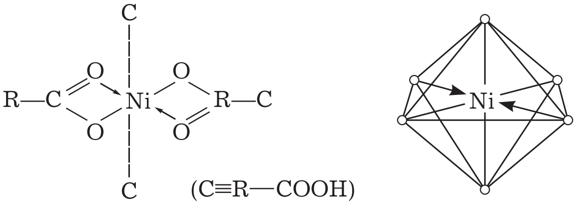


Fig. 1. Structure of nickel naphthenate.

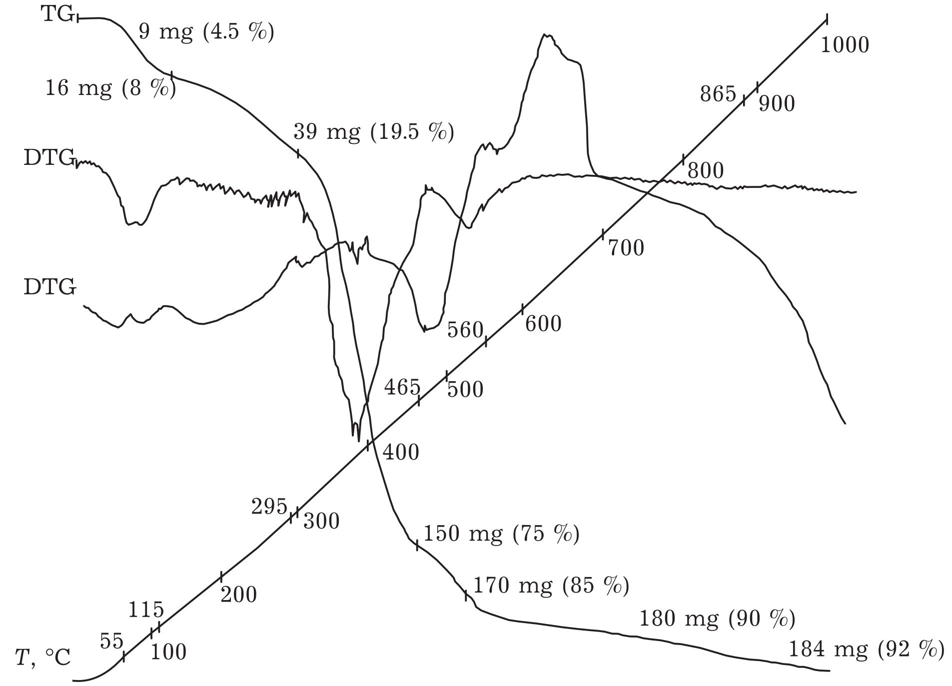


Fig. 2. Derivatogramm of cobalt naphthenate.

the duration of analysis of 100 min, a heating rate of 10 °C/min, the reference standard is Al_2O_3.

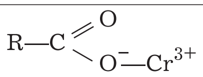
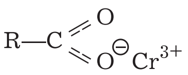
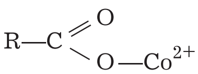
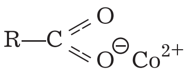
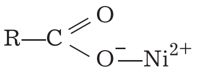
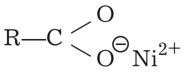
There have been acquired the following results:

i) The obtained salt, *i.e.* Ni(II)-naphthenate, has a diamagnetic structure in the form of an oblong octahedron, which lies on the axial axis (Fig. 1).

This structure persists up to 140–160 °C. Using spectroscopic methods, it was found that water molecules did not surround Ni^{2+} ion as ligands (Fig. 2).

TABLE 1

Infrared spectral data of naphthenates in a *n*-heptane solution

Samples	Type of complexes in octahedral coordination	Wave number, cm^{-1}				Intensity
		δ_{C-H}	ν_s^{COO}	ν_{as}^{COO}	$\nu_{C=O}^{naphth}$	
Cr naphthenate d^3	 $R{-}C\begin{matrix}{/\!\!/}O\\ \diagdown O^{-}{-}Cr^{3+}\end{matrix}$	1385	1450	1595	1700	Weak
	 $R{-}C\begin{matrix}{/\!\!/}O\\ {\diagdown\!\!\diagdown} O^{\ominus}\,Cr^{3+}\end{matrix}$	1420	1470	1605	1710	Intensive
Co naphthenate d^7	 $R{-}C\begin{matrix}{/\!\!/}O\\ \diagdown O{-}Co^{2+}\end{matrix}$	1385	1450	1598	1690	Weak
					1700	»
	 $R{-}C\begin{matrix}{/\!\!/}O\\ {\diagdown\!\!\diagdown} O^{\ominus}\,Co^{2+}\end{matrix}$	1415	1475		1710	Medium
Ni naphthenate d^8	 $R{-}C\begin{matrix}{/\!\!/}O\\ \diagdown O^{-}{-}Ni^{2+}\end{matrix}$	1380	1460	1590	1700	Intensive
		1425	1470	1600		
	 $R{-}C\begin{matrix}\diagup O\\ \diagdown O^{\ominus}\,Ni^{2+}\end{matrix}$					

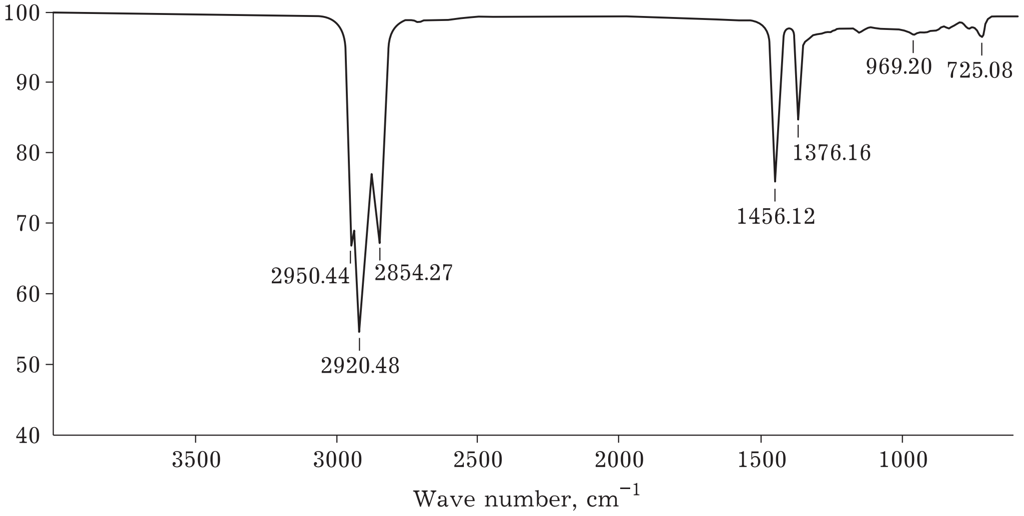


Fig. 3. IR spectrum of dearomatized naphthenic concentrate.

ii) According to reflectance and transmittance spectra, it was determined that CO^{2+} was found in the tetrahedral coordinate.

iii) Chromium(III) naphthenate in a heptane solution is a octahedral complex. Ligand composition of the surroundings proves the likelihood of two types of close structures.

Table 1 gives the composition and structure of the synthesised catalysts.

Thermal analysis of catalyst samples (cobalt and chromium naphthenates) demonstrated that these salts began to lose in mass 19–19.5 % at 300 °C, preserving the main atomic mass, and could be used as catalysts during liquid-phase oxidation of alkanes

Methylcyclohexane with the following physicochemical properties (a colourless liquid, boiling point of 101 °C, melting point of 126.3 °C, a density of 0.77 g/cm^3); and naphthenic concentrate (C_2–C_3 alkyl radical): n_D^{20}= 1.4860, d_4^{20} = 0.8891, kinematic viscosity at

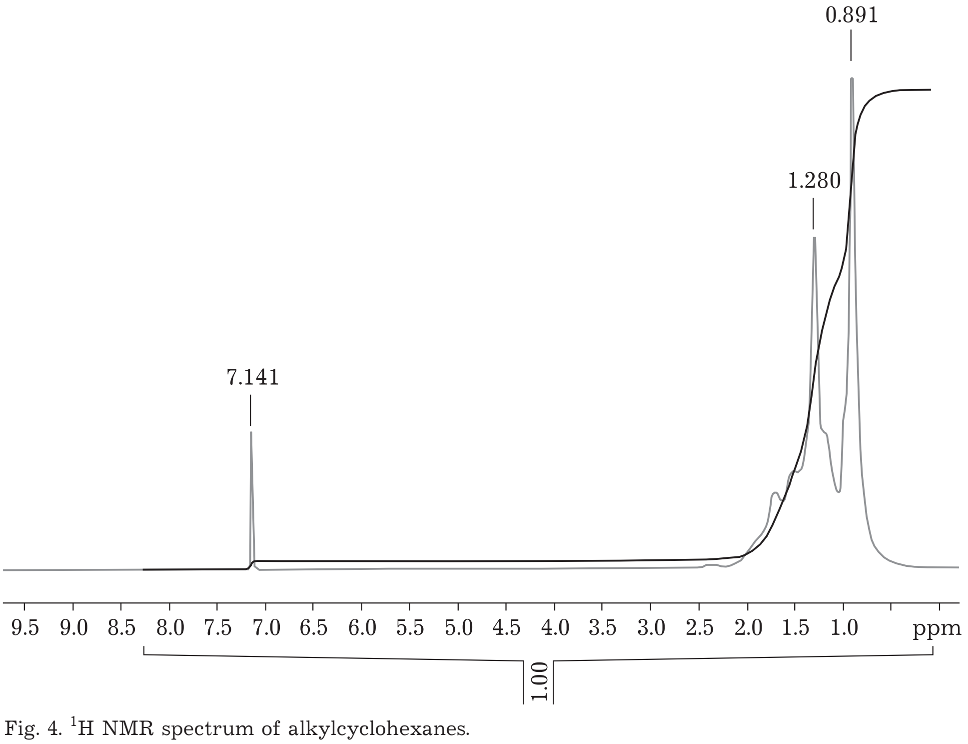


Fig. 4. ^{1}H NMR spectrum of alkylcyclohexanes.

20 °C, mm^2/s, of 8.89, boiling point of 220–260 °C, average molecular mass of 240.5) were used as initial raw materials.

In the spectrum of naphthenic concentrate, absorption bands (AB) with maxima near ν = 2952 and 2923.5 cm^{-1}, responsible for absorption of CH_2 groups in six-membered naphthenic structures, were identified (Fig. 3). Absorption bands of aliphatic CH_3 and CH_2 groups appeared in the spectral range near ν = 1376 and 1458 cm^{-1} as narrow bands.

The number of saturated rings (K_s) is 3.09, there are no aromatic rings, aromaticity is $2 \cdot 10^{-4}$, the fraction of methyl groups in alkyl radicals is 40.7, as demonstrated by NMR spectral analysis of naphthenic concentrate (Fig. 4).

The content of naphthenic hydrocarbons exceeds 79.4 %; from 20 to 20.6 % falls on the fraction of alkyl fragments (C_{alk}).

Liquid-phase oxidation of alkylcyclohexanes was carried out in a bubbling type laboratory reactor (39 cm in length, 3.5 cm in diameter, made of Pyrex glass) equipped with a reflux condenser, thermometer, feed unit of raw materials, sampling and air flow measurement, at atmospheric pressure. A Schott glass filter that ensures an even air distribution over the entire cross section of the column was soldered in the bottom part of the oxidation reactor. Column reaction area is equipped with winding, heating of which is regulated by a laboratory transformer. Air consumption is maintained at a level of 250–300 L/h and the reaction temperature is 95–140 °C.

Oxygen-containing reaction products were determined both analytically and spectrally.

Oxidation was carried out by air oxygen for 5 h in the presence of samples of the prepared catalysts. The number of the used catalysts was (2–3) · 10^{-3} mol/L.

The content of hydroperoxide groups, the yield of the oxidate, NA and oxy-naphthenic acids (ONA), the acidic number of NA and ONA, and also the concentration of hydroxyl groups were determined by the iodometric method.

RESULTS AND DISCUSSION

The joint use of two catalysts that are different by the central Me atom with the same ligand surroundings is of apparent interest. It is known that oxidation of naphthenes is notably accelerated in the presence of Cr and Ni compounds, however, it is shifted towards the formation of mainly oxide during the addition of Co species. Oxidation of methylcyclohexane (1-MCH) was performed in the presence of chromium naphthenate at 95 °C. It is worth noting that naphthenates are ideally dissolved in initial raw materials, while reaction mixture colour varies depending on initial salt colouring.

As demonstrated in [12], it is possible to accumulate a significantly greater amount of hy-

TABLE 2

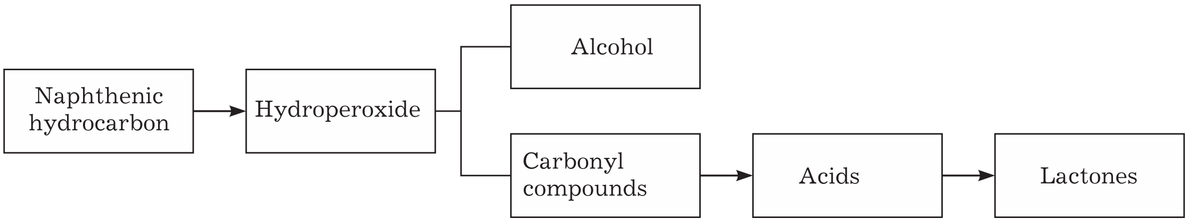
Results of oxidation of alkylcyclohexanes in the presence of transition metal naphthenates

(T = 135–140 °C, air supply rate of 300 L/(kg · h); reaction time of 5 h)

Exp. number	Initial material	Catalyst/ Content, %	Oxidate			Naphthenic acids		Oxy-naphthenic acids	
			AN, mg KOH/g	Yield, %	HP, %	AN, mg KOH/g	Yield, %	AN, mg KOH/g	Yield, %
1*	1-MCH	Ni(napht)/0.2	–	97.2	12	–			
2*	»	Cr(napht)/0.2	–	96.9	19	–	–		
3*	»	Co(napht)/0.3	–	97.8	15	–	–		
4	AlkylC_2,C_3-cyclohexanes	Cr(napht)/0.2	46.0	98.2		130.7	15.0	112.7	13.7
5	»	Cr/Co = 3 : 1 /(0.15 + 0.05)	49.7	97.6		131.1	10.3	108.0	8.3
6	»	Co(napht)/0.3	48.2	98.4		130.0	9.7	117.2	30.6

Note. 1-MCH is methylcyclohexane, AN is acid number, HP is hydroperoxide.

*Reaction temperature 95 °C, duration 5.0 h.



Scheme 1.

droperoxides in oxidation products during liquid-phase oxidation of cycloalkanes with methyl substituents than in case of C_5 and C_6 cycloalkanes. This phenomenon is related to different stabilities of hydroperoxides of two types (chair and boat) [13].

Table 2 gives the results of oxidation of cycloalkanes with air oxygen in the presence of transition metal naphthenates.

As can be seen from the data of Table 2, losses during oxidation are insignificant, in other words, the yield of the oxidate is 97.0–98.4 %. The reaction temperature during oxidation of 1-MCH did not exceed 95 °C and the prevailing components of reaction products under these conditions were hydroperoxides (Scheme 1).

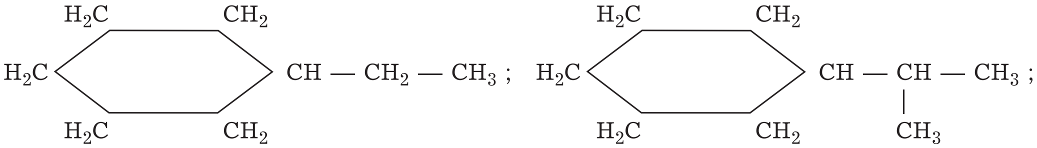
In a series of the tested naphthenates, Cr and Co naphthenates containing hydroperoxides in the amount of 19 and 15 %, respectively, are most active. In this regard, oxidation of a mixture of alkylcyclohexanes at 135–140 °C was carried out in the presence of chromium and cobalt naphthenates, as well as their mixture with Cr/Co = 3 : 1 cation ratio. The content of hydroperoxides in the oxidate is maximum (19 %) during oxidation of 1-MCH in the presence of chromium naphthenate. There is the same tendency during oxidation of ethyl- and propylcyclohexanes. In this case, the yield of NA is 15 % (Scheme 2).

The introduction of cobalt naphthenate into the system leads to a notable decrease in the yield of NA, however, the yields of oxy-acids containing carboxyl and hydroxyl groups are substantially increased (more than 30 %). This is the reaction shift indicator towards the greater formation of oxy-acids in case of the use of a Co-containing catalyst. To achieve the maximum yield of NA, the optimum content of chromium naphthenate is 0.2 mass %, while that of cobalt naphthenate (for the maximum yield of ONA) is 0.3 %.

There are also other aspects of catalyst behavior in the oxidizing system. It is worth considering that association of catalyst salt species into micelles may proceed during oxidation. Catalyst activity depends on the catalyst molecule combination. If a catalyst generates a regular solution, chain initiation rate should increase linearly with its concentration rise. It is certified that particle number in a volume unit increases proportionally to catalyst concentration but is almost terminated with increasing the concentration of the dissolved salt. However, afterwards, particle quantity increase slows down and is almost terminated, as a further increase in catalyst concentration leads to a rise in the volume of the micelles. Apparently, all these points somewhat explain the difference in activities of the catalysts used.

Figures 5 gives IR spectra of reaction products *via* experiments No. 1, 4, and 5 (see Table 2).

As can be seen from the presented spectra in the presence of Ni naphthenate (experiment 1) in the oxidate, there are no AB near 939 and 1707 cm^{-1}, typical for carboxyl groups. In IR spectra of NA (experiments 4 and 5, see Ta-



Scheme 2.

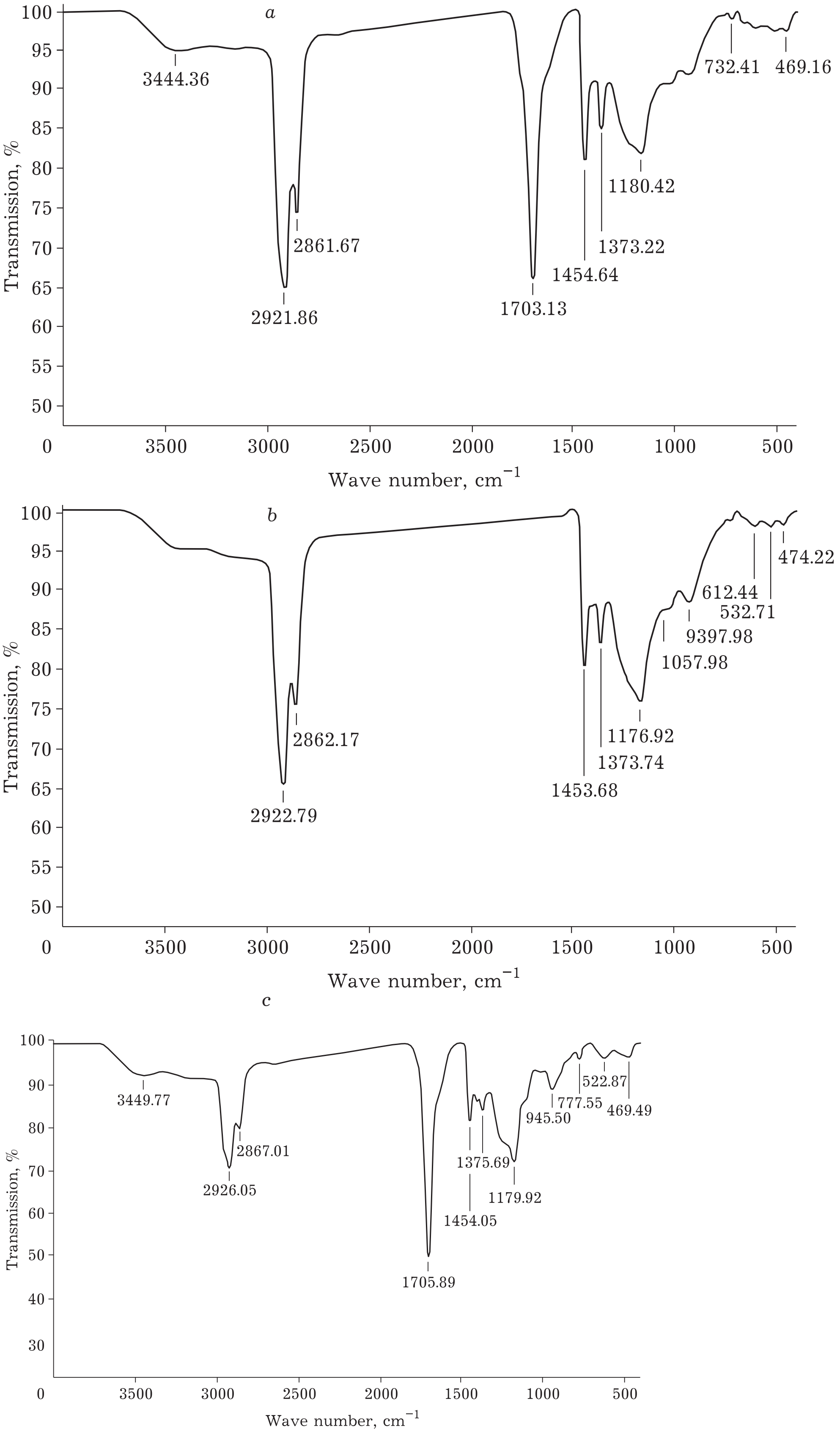


Fig. 5. IR spectra: *a*, *c* – naphthenic acids (see Table 2, experiments 4 and 5, respectively), *b* – oxidate (experiment 1).

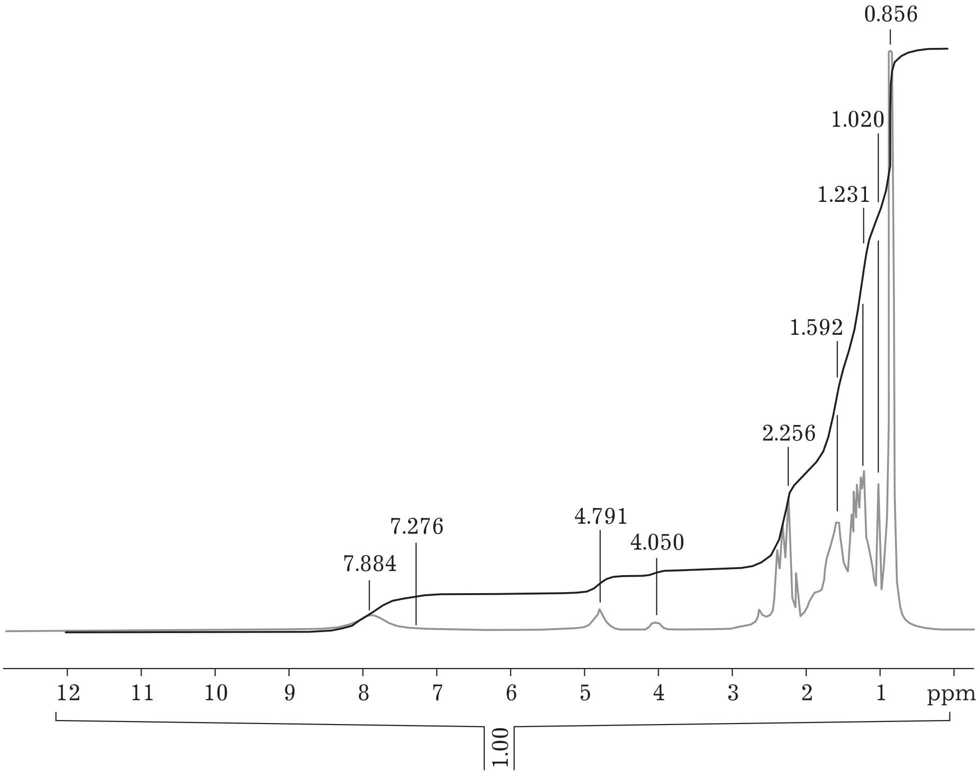


Fig 6. ^{1}H NMR spectrum of naphthenic acids prepared in the presence of Cr and Co naphthenates (experiment 5).

ble 2), there are AB near 945 см$^{-1}$, corresponding to the deformation vibrations of the O–H bond in the carboxyl group (COOH), AB near 1705 cm^{-1} of the C=O bond in the acid species, near 1179 cm^{-1} of the C–O bond, and near 3449 cm^{-1} of the stretching vibrations of the O–H bond.

Figure 6 gives the ^{1}H NMR spectrum of NA obtained in the presence of a mixture of Cr and Co naphthenes. In the spectrum, there are signals of CH_2 group located in the α-position to the COOH functionality (2.26 ppm (15.4 %)); and those of the COOH group (7.88 ppm (6.4 %)). Hydrogen distribution along the structural groups is as follows: H_γ – 0.86 ppm (30.9 %), H_n – 1.59 ppm (20.9 %); H_p – 1.23 ppm (26.4 %).

The finding attests to the fact that only hydroperoxides and to a lesser degree alcohols are generated during oxidation of 1-MCH. Oxidation of alkylcyclohexanes with longer radicals (C_2, C_3) was carried out at elevated temperatures (to 140 °C), with the result that naphthenic acids (up to 15 %) combined with oxy-acids (up to 40 %) were synthesised in significant amounts (experiment 6). Thus, resulting from the reaction, the naphthene ring does not decompose, while carboxyl groups in side chains shift in relation to the naphthene cycle.

CONCLUSION

1. Chromium, nickel, and cobalt naphthenates have been synthesised by preliminary leaching of technical naphthenic acids in the presence of solvents.

2. Physicochemical, thermogravimetric, and spectral characteristics of chromium, nickel, and cobalt naphthenates have been studied.

3. Liquid-phase oxidation of methylcyclohexane and a mixture of alkylcyclohexanes was carried by air oxygen out in a bubbling-type reactor.

4. The introduction of cobalt naphthenate into the system leads to a marked reduction in the yield of naphthenic acids. However, the content of oxy-acids increases considerably (more than 30 %).

5. To achieve the maximum yield of naphthenic acids, the optimum content of chromium naphthenate is 0.2 mass %, while that of oxy-naphthenic acids requires cobalt naphthenate content of 0.3 %.

6. Carboxyl groups are found in side chains in relation to the naphthene cycle, as demonstrated by analysis of ^{1}H NMR spectra of naphthenic acids (Cr/Co = 3 : 1 catalysts, total content of 0.2 mass %).

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