comparison with higher numbered groups (Fig. 2). A further increase in n, in general, is correlated with a small increase of these values although in some cases the variation was comparable to calculation errors. The contribution of the entropy component to the differential molar free energy of sorption on the introduction of the first CF_2 group comprised up to 70% of the enthalpy contribution at 100°C and the contribution of the remaining CF_2 groups ~60%. The relationship of the entropy and enthalpy components was approximately the same for both SPs. This dependence agrees with the previously discussed change of ΔG_n (CF_2) in the series of pseudohomologs [1]. As the polyfluoroalkyl chain lengthens the interaction of the CF_2 group with the molecules of the SP is strengthened and at the same time the number of degrees of freedom of molecular rotation is increased.

For CF_2 groups with the same number but belonging to a series of ester homologs with varying length of the alkyl chain R, the values of ΔH_n (CF_2) and ΔS_n (CF_2) are smaller the longer R is. To a certain degree this agrees with the change in ΔG_n (CF_2) in the above series (see Fig. 2). However, if the values of ΔG_n (CF_2) for homologs with R = C_5H_{11} and C_6H_{13} are close and at 100°C differ from one another within the limits of 0.1 kJ/mole, then the differences in the values of ΔH_5 (CH_2) reach ~0.5 kJ/mole and of ΔS_5 (CF_2) 1.0-1.3 J/(mole·deg).

Thus, the strengthening of the interaction of the alkyl chain of a saturated, fluorinated carboxylic acid ester with the SP is accompanied by a weakening of the molecular interactions of the fluorinated group with this phase.

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BIOMIMETIC ACTIVATION OF THE C–H BOND.

1. OXYGENATION OF HYDROCARBONS BY ATMOSPHERIC OXYGEN IN THE PRESENCE OF METAL CHLORIDES AND ASCORBIC ACID OR GLUCOSE

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Oxygenation of hydrocarbons by atmospheric oxygen is initiated by $FeCl_3$, $CuCl_2$, and $NaAuCl_4$ in aqueous acetonitrile in the presence of ascorbic acid or glucose as the reducing agent. Cyclohexane is oxidized to cyclohexanol and cyclohexanone in the presence of ascorbic acid. Ethylbenzene forms acetophenone and 1-phenylethanol in the presence of ascorbic acid or glucose. Styrene is oxidized to form benzaldehyde in general.

Chemical modeling of the action of oxidation–reduction enzymes, in particular biomimetic activation of the C–H bond [1-6], is very important not only because it provides a better understanding of the mechanism of oxidation of different substances in the living cell, but also because such studies could lead to new selective processes for refining saturated, olefinic, and aromatic hydrocarbons. It is well-known that monooxygenase enzymes oxidize substrates (S) according to the scheme:

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$$S + O_2 + AH_2 \rightarrow SO + A + H_2O,$$

where AH_2 is a hydrogen-atom donor, such as NADH or NADPH. Monooxygenases, as a rule, contain ions of iron, more rarely of copper. A flavine or pteridine fragment has a key role in certain monooxygenases during oxidation [7-9].

One of the first chemical models of monooxygenases, proposed by Udenfriend [10], consists of O_2, Fe^{2+} ions, ascorbic acid, and EDTA. The reaction was carried out in aqueous solution: the benzene ring in acetanilide, quinoline, and certain other aromatic compounds was hydroxylated. This system has been used [11] to oxidize cyclohexane in a heterogeneous aqueous-acetone mixture; an oxenoid mechanism has been suggested for the process [12], according to which an oxenoid species Fe···O=O (similar to the carbenoid species, which is able to transfer a divalent carbon atom) attacks the substrate resulting in formation of SO and, for example, the FeOH moiety. However, an alternative mechanism was also considered in which oxidation of the substrate occurs during attack by a hydroxyl radical. A system has recently been described which hydroxylates alkanes and contains O_2, Ru^{3+}, EDTA, and ascorbic acid [13]; another system, Cu^{2+}–ascorbic acid–O_2, hydroxylates benzene [14] (see also new research in this field [15]). It should be noted that yields of oxidation products in Udenfriend's system and analogous systems rarely exceed 100% calculated per mole of metal. In [13] the yield of cyclohexanol during oxidation of cyclohexane reached 5 moles per mole of Ru(III) and ~2 moles of phenol per mole of Cu^{2+} are formed during hydroxylation of benzene in the presence of Cu^{2+} [14].

It was of interest to study oxygenation of hydrocarbons in homogeneous solution, in an organic solvent able to dissolve different types of compounds: alkanes, arylalkanes, and olefins. For the metal-complex catalysts it was reasonable to use salts of iron and copper, which are known to be capable of coordinating and activating O_2, and also of gold as an analog of copper.

EXPERIMENTAL

All reactions were carried out in air in closed light-tight vessels at ~20°C with magnetic stirring. Samples were taken at selected intervals of time then analyzed by GLC on an LKhM-80-6 chromatograph (sorbent INERTON AW-HMDS 0.2-0.315 mm, impregnated with 5% Carbowax; column length 2 m; argon carrier gas). The results obtained are shown in Table 1.

RESULTS AND DISCUSSION

In this work the catalytic action of Fe(III), Cu(II), Cu(I), and Au(III) chlorides was studied in a system analogous to Udenfriend's system; reactions were carried out at ~20°C in aqueous acetonitrile ($CH_3CN:H_2O$ = 8.5:1 by volume). Benzene, cyclohexane, ethylbenzene, and styrene were chosen as substrates ([S] = 0.46 moles/liter). The catalysts used were $FeCl_3$, $CuCl_2$, and $NaAuCl_4$ at a concentration of $5.0 \cdot 10^{-4}$ mole/liter with ascorbic acid (10^{-2} mole/liter) as the reducing agent. Usually the buildup of oxidation products with time was followed, as shown in Fig. 1 for catalysis by the $AuCl_4^-$ ion.

Phenol is formed from benzene during catalysis with metal chlorides, $FeCl_3$ being the most active in this reaction ($1.4 \cdot 10^{-3}$ mole/liter phenol in 96 h). Yields of phenol in the case of $CuCl_2$ and $NaAuCl_4$ were lower ($4.5 \cdot 10^{-4}$ and $3.5 \cdot 10^{-4}$ mole/liter, respectively) for the same period of time. Cyclohexane gives small yields of cyclohexanol and cyclohexanone (in 4 h, for $FeCl_3$ $2.4 \cdot 10^{-4}$ and 10^{-4} mole/liter, respectively; for $CuCl_2$ $3.5 \cdot 10^{-4}$ and 10^{-4}; for $NaAuCl_4$ $1.5 \cdot 10^{-4}$ and $0.5 \cdot 10^{-4}$). In the presence of $CuCl_2$ n-hexane is oxidized very slowly to give, after five days, mainly hexanol-1 ($0.6 \cdot 10^{-5}$ mole/liter), hexanol-2 ($1.8 \cdot 10^{-5}$ mole/liter), and hexanol-3 (10^{-5} mole/liter). In every case the amount of alcohol is considerably greater than the amount of ketone. The pattern is reversed during oxidation of ethylbenzene: for the $CuCl_2$ and $AuCl_4^-$ catalysts the ketone/alcohol ratio is ~2 (the yields after 3 h of 1-phenylethanol and acetophenone are $1.1 \cdot 10^{-3}$ and $2.5 \cdot 10^{-3}$ mole/liter, respectively, for Cu and $0.8 \cdot 10^{-3}$ and $2.4 \cdot 10^{-3}$ mole/liter for Au), but in the case of $FeCl_3$ only acetophenone is produced ($1.2 \cdot 10^{-3}$ mole/liter). The reaction is inhibited by addition of o-phenanthroline; after 24 h no oxidation products were found in the case of $AuCl_4^-$, and in the case of $FeCl_3$ and $CuCl_2$ only a small amount of acetophenone is formed ($5.6 \cdot 10^{-4}$ and $4.2 \cdot 10^{-4}$ mole/liter, respectively). Addition of the disodium salt of EDTA ($5.0 \cdot 10^{-4}$ mole/liter) to a solution of $FeCl_3$ and ascorbic acid leads to slight decrease in the yield of acetophenone ($6.0 \cdot 10^{-4}$ mole/liter after 24 h). Oxidation of styrene yields mainly benzaldehyde. Thus, the yields after 2 h in the presence of $FeCl_3$

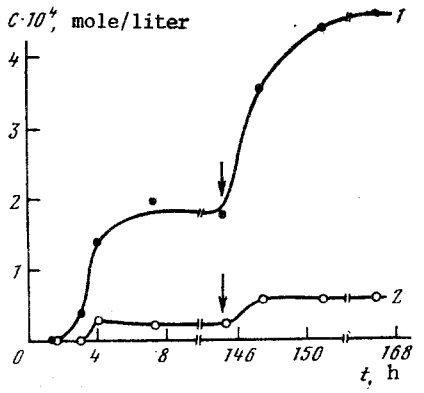

Fig. 1. Kinetic curves for build-up of cyclohexanol (1) and cyclohexanone (2) during oxidation of cyclohexane ($4.6 \cdot 10^{-1}$ mole/liter) by atmospheric oxygen in the presence of ascorbic acid ($2.5 \cdot 10^{-3}$ mole/liter) and $NaAuCl_4$ ($5.0 \cdot 10^{-4}$ mole/liter) in a CH_3CN–H_2O mixture (8.5:1 by volume). Addition of $2.5 \cdot 10^{-3}$ mole/liter of ascorbic acid is marked by arrows.

TABLE 1. Simultaneous Oxygenation of Ethylbenzene and Cyclohexane by Oxygen in the Presence of Ascorbic Acid and Metal Chlorides (reaction time 40 h)

Metal chloride	1-Phenylethanol* / Acetophenone	Cyclohexanol* / Cyclohexanone	Ψ
$FeCl_3$	0,2	3,8	6,3
$CuCl_2$	0,1	1,2	6,5
$CuCl$	0,3	9,4	3,4
$NaAuCl_4$	1,0	2,1	4,8

*Mole ratio of reaction products.

or $NaAuCl_4$ are $1.7 \cdot 10^{-3}$ or $7.0 \cdot 10^{-4}$ mole/liter of benzaldehyde, respectively, together with traces of styrene oxide and acetophenone, and after 4 h in the presence of $CuCl_2$: $4.2 \cdot 10^{-4}$ mole/liter of benzaldehyde, $1.6 \cdot 10^{-4}$ mole/liter of styrene oxide, and $0.4 \cdot 10^{-4}$ mole/liter of acetophenone.

It should be noted that in the absence of metal chlorides hydrocarbons are oxidized very slowly by atmospheric oxygen under the action of ascorbic acid (10^{-2} mole/liter). Thus, after 18 days cyclohexane yields $4.8 \cdot 10^{-4}$ mole/liter of cyclohexanol and $1.6 \cdot 10^{-4}$ mole/liter of cyclohexanone. However, after 1 day the concentration of oxidation products is $<10^{-5}$ mole/liter. After 18 days ethylbenzene yields $5.4 \cdot 10^{-4}$ mole/liter of 1-phenylethanol and $1.8 \cdot 10^{-4}$ mole/liter of acetophenone. It is assumed that in these experiments the oxidation is catalyzed by subanalytical amounts of metal ions present in the solvents and the reagents [16-19].

Ascorbic acid may be replaced in the oxidation reactions by D-glucose (10^{-2} mole/liter in all the experiments); however, then only ethylbenzene is oxygenated and cyclohexane and styrene do not react. The highest activity is displayed by $CuCl_2$ ($5.0 \cdot 10^{-4}$ mole/liter). After 2.5 h ethylbenzene yields $1.7 \cdot 10^{-3}$ mole/liter of acetophenone and $1.6 \cdot 10^{-3}$ mole/liter of 1-phenylethanol. Following this there is a slow build-up of acetophenone and a decrease in 1-phenylethanol concentration. Both processes are completed after 19 days, when the concentrations of ketone and alcohol are $4.4 \cdot 10^{-3}$ and 10^{-4} mole/liter, respectively. In an analogous reaction in the presence of $NaAuCl_4$, $1.6 \cdot 10^{-3}$ mole/liter of ketone and $1.6 \cdot 10^{-3}$ mole/liter of alcohol are formed after 2.5 h, the yields of acetophenone and 1-phenylethanol reaching $2.6 \cdot 10^{-3}$ and $2.2 \cdot 10^{-3}$ mole/liter respectively after 14 days. Oxidation scarcely occurs in the presence of $FeCl_3$ but no reducing agent (after 24 days only $8.0 \cdot 10^{-5}$ mole/liter of acetophenone was detected in the reaction mixture).

We also carried out a simultaneous competitive oxidation of cyclohexane and ethylbenzene with a view to determining the nature of the hydroxylating species. The data

obtained are given in Table 1. In addition to the alcohol/ketone ratio for each substrate, we also give values of the parameter Ψ which is defined as follows:

$$\Psi = 6([C_6H_5CHOHCH_3] + [C_6H_5COCH_3]) / ([C_6H_{11}OH] + [C_6H_{10}O]).$$

This parameter may be used to characterize the reactivity of an oxygenating reagent with respect to one H atom in ethylbenzene and cyclohexane CH_2 groups.

The values of Ψ determined for oxygenation in the presence of the four chlorides are only slightly higher than the values of Ψ obtained for the reaction of hydrocarbons with OH^- free radicals: 2.9 for oxygenation using H_2O_2 during UV photolysis and 3.6 for hydroxylation with Fenton's reagent.

Thus, chlorides of different metals (Fe, Cu, and Au) in general have a different effect on the oxygenation of hydrocarbons by oxygen; this is consistent with a reaction mechanism in which the active species are not free hydroxyl radicals but complexes of reduced metal ions with an oxygen molecule, in which the moiety attacking the C–H bond has a radical-like character.

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