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Oxidation of 1,4-dimethylcyclohexane by perchloric acid catalyzed by polyphenylferrosiloxane

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The reaction of oxidation of 1,4-dimethylcyclohexane (DMCH) by perchloric acid at ~ 20 °C catalyzed by polyphenylferrosiloxane has been found. The chromatographic analysis has revealed the formation of several products, including the tertiary alcohol with 100% retention of the configuration of the initial configuration. The specific feature of the process is the following: along with the high stereospecific formation of the tertiary alcohol, *cis*-*trans* isomerization in the starting 1,4-DMCH is observed. The data obtained are discussed on the basis of the mechanism, including the formation of a ferryl intermediate with the subsequent transfer of the oxygen atom to the tertiary C--H bond of 1,4-DMCH through the intermediate complex with the five-coordinated carbon.

Key words: oxidation of hydrocarbons, perchloric acid, polyphenylferrosiloxane, ferryl intermediate, five-coordinated carbon.

Many researchers are interested in the functionalization of alkanes involving metallocomplexes.¹⁻³ Recent works have shown that high-valent oxo derivatives of metals (including Fe) can transfer oxygen, inserting it at the C-H bond without intermediate formation of free radicals. This mechanism suggests the formation of an intermediate complex with five-coordinated carbon,*

* The possibility of a complex with five-coordinated carbon was theoretically substantiated^{4,5} and then experimentally confirmed⁶ by XDA of the complex of heptane with neutral Fe^{II} porphyrin in which the Fe--C bond length is equal to 2.5 Å, *i.e.*, carbon has coordination number 5. whose characteristic feature is the structural nonrigidity, which can appear as partial isomerization of the products.

The high-valent metal oxo complexes can evidently exhibit different reactivities. It cannot be ruled out that the least active complexes react reversibly with hydrocarbons to result in the isomerization of the latter without insertion of oxygen at the C—H bond. The reaction described hereinafter probably belongs precisely to this type.

We observed that at ~ 20 °C 1,4-dimethylcyclohexane (DMCH) is slowly oxidized by perchloric acid in MeCN in the presence of the iron complex, polyphenyl-

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Entry	Composition of the system ^a	Substrate ^b	Time of interaction	Yield of tertiary alcohol ^c /mmol L ⁻¹	Degree of isomerization ^d (%)
1	PPFS + HClO ₄	trans-DMCH	15 days 30 days	0.6 (100% trans) 1.3 (100% trans)	0.05 0.08
23	$\frac{PPFS + HClO_4}{PPFS/Ar}$	cis-DMCH cis-DMCH	30 days 30 days	1.2 (100% cis) <0.1	0.11 <0.01
4	PPFS	trans-DMCH	15 days	<0.1	0.01
	HCIO	trans-DMCH	15 days	<0.1	<0.01
6	$PPFS + HClO_4 + H_2O_2$ $PPFS + HClO_4 + H_2O_2$	trans-DMCH	l h	2.5 (60% trans)	0.05
7		cis-DMCH	l h	7 (39% cis)	0.16
8	$\frac{Fe(cyclam)(OTf)_2 + PhIO}{Fe(cyclam)(OTf)_2 + PhIO}$	trans-DMCH	lh	4 (90% trans)	-0.01
9		cis-DMCH	lh	8 (98% cis)	0.06

Table 1. Oxidation and isomerization of 1,4-DMCH under different conditions

^a All experiments were carried out in MeCN (purified by a standard procedure) in air, except entry 3 performed in an atmosphere of Ar, at 20 °C. In entries 1-5, [PPFS] = 20 mmol L^{-1} , [HClO₄] = 120 mmol L^{-1} ; in entries 6 and 7, [PPFS] = 2 mmol L^{-1} , [HClO₄] = 120 mmol L^{-1} ; in entries 6 and 7, [PPFS] = 2 mmol L^{-1} , [HClO₄] = 48 mmol L^{-1} , [H₂O₂] = 100 mmol L^{-1} ; in entries 8 and 9, [Fe (cyclam)(OTf)₂] = 4 mmol L^{-1} (cyclam is 1,4,8,11-tetraazacyclotetradecane, OTf is CF₃SO₃⁻, triflate), [PhIO] = 50 mmol L^{-1} . ^b In entries 1-5, [trans-DMCH] = [cis-DMCH] = 170 mmol L^{-1} ; in entries 6-9, [trans-DMCH] = 170 mmol L^{-1} , [cis-DMCH] = 70 mmol L^{-1} .

^c The yield of isomers of the tertiary alcohol with the *cis*- and *trans*-orientation of the methyl groups was determined by GLC on a Hewlett Packard 5880A chromatograph, column DB-WAX, l = 60 m. The percentage content of the alcohol that retained the configuration of the starting substrate is given in parentheses.

^d The starting *cis*-1,4-DMCH contained 0.50% *trans*-isomer, and the starting *trans*-1,4-DMCH contained 0.22% *cis*-isomer (the error of chromatographic analysis was not greater than 0.01%). The increase in the content of the *cis*-isomer upon the oxidation of *trans*-DMCH and that of the *trans*-isomer upon the oxidation of *cis*-DMCH during the reaction are given in percent of the initial concentration of the substrate.

ferrosiloxane (PPFS)* (Table 1, entries 1 and 2), giving the tertiary alcohol with 100% retention of the configuration and several other products (detected by gas chromatography) except secondary and primary alcohols. The tertiary alcohol is accumulated with a constant rate during some time (entry 1), then its amount decreases, and the composition and ratio of the other products also change in time. The presence of the iron complexes and HClO₄ is necessary for the reaction considered, and the products are not formed in the absence of one of these compounds (entries 4 and 5). The replacement of air by argon has no effect on the amount and composition of the products in entries 1 and 2.

The cis-trans-isomerization of the initial substrate was observed in parallel with the appearance of the tertiary alcohol (see Table 1, entries 1-5), *i.e.*, an increase in the amount of the cis-isomer when trans-DMCH was used and trans-isomer when cis-DMCH was used. The degree of isomerization was estimated from the change in the ratio of the cis/transisomers during the reaction. As can be seen in Table 1,

* The main structural fragment of PPFS (-Si(R)-O-Fe-O-Si(R)-O-, R is phenyl) consists of

the isomerization occurs under the same conditions as the formation of the oxidation products. In the absence of HClO₄ and in the presence of the atmospheric oxygen (see entry 4), the *cis/trans*-DMCH ratio differs only insignificantly from the initial one (this difference varies within the experimental error). No isomerization is observed in the absence of O₂ and HClO₄ (entry 3) and PPFS (entry 5).

As entry 5 shows, HClO₄ is unable to oxidize hydrocarbon under mild conditions. In the presence of the iron complex (PPFS), the O atom is most likely transferred from HClO₄ to the Fe ion, which results in the formation of a ferryl intermediate (Fe=O), which can^{9-11} oxidize the C—H bonds in the substrate without intermediate formation of alkyl radicals. This is evidenced by 100% retention of the configuration in the tertiary alcohol.

The amount of the tertiary alcohol is up to 10% of the decrease in the substrate. Other products, not identified yet, are formed along with the alcohol. Probably, these products appear due to the nonselective oxidation of DMCH by oxidants (HClO₃ and others) stronger than HClO₄, which are formed due to the transfer of the O atom from HClO₄ to PPFS.

Evidently, the isomerization observed in entries 1 and 2 cannot be explained by the intermediate formation of tertiary alkyl radicals, because isomers of the tertiary alcohols were not observed in the products, unlike the experiments on radical oxidation (entries 6 and 7).¹² On the other hand, in entries 8 and 9 where the mechanism of oxidation involving the ferryl inter-

siloxane chains with covalently-linked iron atoms.⁷ The synthesis and structure of PPFS have been described previously.⁸ The PPFS used in the work had the following compositions: Si, 9.5%; Fe, 29.4%; Si/Fe = 1.56.

mediate is most probable,¹³ only insignificant isomerization of the substrate is observed. The close isomerization rates for *cis*- and *trans*-DMCH in entries 1 and 2 indicate that this phenomenon cannot be explained by substantially different reactivities of the *cis*- and *trans*tertiary C—H bonds in the PPFS-system (*cf.* Ref. 14). Entry 5 shows that the isomerization is not a result of the acid catalysis. Nevertheless, it can be assumed that PPFS possesses some properties of aprotic acid and enhances the effect of the protic acid HClO₄, *i.e.*, HClO₄ acts as a catalyst of isomerization only in the presence of PPFS. However, the weak coordinating ability of ClO₄⁻ is an argument against this assumption.

The absence of satisfactory trivial explanations of the isomerization forced us to consider a mechanism suggesting the formation of an intermediate complex of the oxidant with the substrate with five-coordinated carbon. For this purpose, the range of assumed properties of this complex should be extended by the assumption that its isomerization is possible not only due to the rotation of the H-H fragment in the CH₂ unit, as mentioned previously,^{4,5} but also due to the rotation of H-R or, which is equivalent, of the R¹-R² fragment of the cyclohexane ring at the tertiary carbon atom (Scheme 1).

Scheme 1



L is the ligand environment of iron and k_i is the isomerization rate constant

The cyclohexane ring fixes the mutual orientation of the hydrocarbon R^1 and R^2 residues, which leads to the possibility of interaction between them and decreases energy expenditures to the rotation of the R^1-R^2 fragment in the complex with five-coordinated carbon.

Scheme 1 explains the experimental results when the rate of decomposition of the complex with fivecoordinated carbon is assumed to be much higher than the rate of hydroxylation of the C-H bond (*i.e.*, $k_{-1} >>$ $k_1 + k_{cis}$, $k_{-2} >> k_1 + k_{trans}$), which corresponds qualitatively to the low activity of the system (*i.e.*, $k_{-1} >> k_1$, $k_{-2} >> k_2$). The ratio of the rate constants $k_{-1} \ll k_i + k_{cis}$, $k_{-2} \ll k_i + k_{trans}$ corresponds to another limiting case, the high activity of the system (the systems in entries 8 and 9 approach this situation), and the isomerization in the intermediate complex is observed only in the products, tertiary alcohols. In the intermediate case, the isomerization occurs simultaneously both in the substrate and product. Perhaps, this case corresponds to the systems in entries 6 and 7 in which the nonradical route occurs along with the radical oxidation.

Thus, in this work, we presented the specific features of the discovered reaction of mild oxidation of alkanes by $HClO_4$ and explained them on the basis of modern concepts on the mechanism of nonradical oxidation of alkanes by oxygen.

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