Pergamon

Tetrahedron 55 (1999) 5345–5358

TETRAHEDRON

Oxidations by the System "Hydrogen Peroxide – Manganese(IV) Complex – Acetic Acid" – Part II.

Hydroperoxidation and Hydroxylation of Alkanes in Acetonitrile

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Received 14 December 1998; revised 4 March 1999; accepted 8 March 1999

Abstract: Higher alkanes (cyclohexane, *n*-pentane, *n*-heptane, methylbutane, 2- and 3-methylpentanes, 3-methylhexane, *cis*- and *trans*-decalins) are oxidized at 20 °C by H_2O_2 in air in acetonitrile (or nitromethane) solution in the presence of the manganese(IV) salt $[L_2Mn_2O_3](PF_6)_2$ (L = 1,4,7-trimethyl-1,4-7-triazacyclononane) as the catalyst. An obligatory component of the reaction mixture is acetic acid. Turnover numbers attain 3300 after 2 h, the yield of oxygenated products is 46% based on the alkane. The oxidation affords initially the corresponding alkyl hydroperoxide as the predominant product, however later these compounds decompose to produce the corresponding ketones and alcohols. Regio- and bond selectivities of the reaction are high: C(1) : C(2) : C(3) : C(4) ≈ 1 : 40 : 35 : 35 and 1° : 2° : 3° is 1 : (15–40) : (180–300). The reaction with both isomers of decalin gives (after treatment with PPh_3) alcohols hydroxylated in the tertiary positions with the *cis*/*trans* ratio of ~2 in the case of *cis*-decalin, and of ~30 in the case of *trans*-decalin (i.e. in the latter case the reaction is stereospecific). Light alkanes (methane, ethane, propane, normal butane and isobutane) can be also easily oxidized by the same reagent in acetonitrile solution, the conditions being very mild: low pressure (1–7 bar of the alkane) and low temperature (–22 to +27 °C). Catalyst turnover numbers attain 3100, the yield of oxygenated products is 22% based on the alkane. The yields of oxygenates are higher at low temperatures. The ratio of products formed (hydroperoxide : ketone : alcohol) depends very strongly on the conditions of the reaction and especially on the catalyst concentration (at higher catalyst concentration the ketone is predominantly produced).

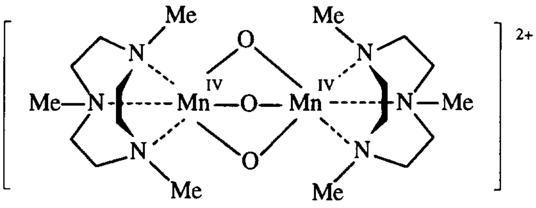
Key words: activation of the C–H bonds, alkanes, butanes, cyclohexane, decalin, ethane, heptane, hydrocarbons, hydrogen peroxide, hydroperoxides, manganese complexes, metal complex catalysis, methane, oxidation, oxygenation, propane, retention of configuration, stereoselective reactions.

It is well known that transition-metal complexes are capable of catalyzing hydrocarbon oxidations [1] by molecular oxygen or/and various oxygen donors, particularly, hydrogen peroxide.[2] Manganese complexes exhibit high activity in catalysis of oxidation of unsaturated and saturated hydrocarbons as well as other organic compounds.[3] High-valent manganese complexes with cyclic nitrogen-containing ligands are among these

PII: S0040-4020(99)00233-1

catalysts.[4] It is interesting that such complexes, especially binuclear manganese derivatives, can be functional models of manganese-containing enzymes: manganese superoxide dismutase, manganese catalase, and photosynthetic oxygen-evolving complex.[5]

Earlier we have found that the dinuclear manganese(IV) complex $[LMn^{IV}(O)_3Mn^{IV}L]^{2+}$ (**1**), where L is 1,4,7-trimethyl-1,4,7-triazacyclononane, used as the hexafluorophoshate salt, catalyzes oxygenation of some alkanes either by peroxyacetic (or less efficiently by 3-chloroperoxybenzoic) acid or by H_2O_2 in the presence of carboxylic acids.[6]



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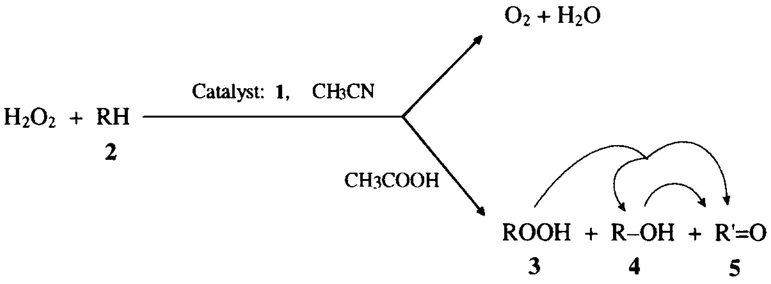
The synthesis of complex **1** has been described by Wieghardt *et al.*[7] (see also work on improved synthesis of complex **1** [8] and preparations of related compounds.[9]

Results and Discussion

We wish to report here the effective oxygenation of saturated hydrocarbons, RH, **2**, by hydrogen peroxide catalyzed by the dinuclear manganese(IV) complex **1** in the presence of acetic acid. The oxidation affords initially the corresponding alkyl hydroperoxide, **3**, as the predominant product, however later these compounds decompose to produce the corresponding alcohols (**4**) and ketones (**5**) (Scheme 1).

Figures 1–5 demonstrate the experimental data on oxidation of cyclohexane by the reagent "hydrogen peroxide – complex **1** – acetic acid". Usually acetonitrile was used as a solvent (Figures 2–5), however the oxidation can be also carried out in nitromethane (Figure 1). Acetic acid is the obligatory component of the oxidizing system since in its absence almost all hydrogen peroxide decomposes to produce molecular oxygen and water (Scheme 1).

The maximum of the initial rate of the oxidation (measured as the concentrations of the oxygenates after 20 min) is approximately at $[CH_3COOH] = 0.5$ mol dm^{-3}, whereas the total yield of cyclohexanol and cyclohexanone is even higher at $[CH_3COOH] = 0.25$ mol dm^{-3} (Figure 2). Typically the reactions were carried out at 20 °C (Figures 1, 2, 4, and 5) although the oxidation at 0 °C also proceeds with high rate (Figure 3). The oxidation of alkanes proceeds with an induction period (a few minutes; the induction period being longer at 0°C) during which the color of the solution changes from pale pink to pale yellow. The subsequent reaction gives rise to the formation of oxygenated products, and the reaction solution gradually becomes almost colorless.



Scheme 1. Different routes of the alkane oxidation by H_2O_2 in the absence and presence of acetic acid.

The reactions were quenched by the addition of solid triphenylphosphine, and GC analysis gave concentrations of cyclohexanol and cyclohexanone as the products. A comparison of alcohol and ketone concentrations (measured by GC) before and after the addition of PPh_3 (the solution untreated with PPh_3 contains alkyl hydroperoxide, ROOH, which completely of partially decomposes in GC to produce ROH, R'=O and other compounds whereas triphenylphosphine quantitatively reduces ROOH to ROH [1a, 10–13]) testifies that alkyl hydroperoxides are formed in the initial period, however they are partially transformed into ketones and alcohols (Figure 4). It is necessary to note that total concentration of the oxygenates (cyclohexanol and

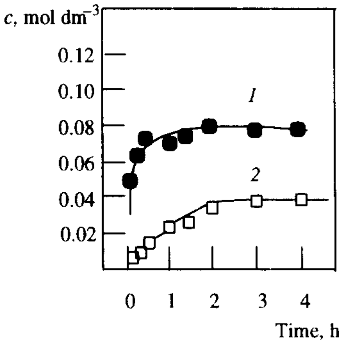


Figure 1. Kinetics of accumulation of cyclohexanol (*1*) and cyclohexanone (2) in the oxidation of cyclohexane (0.46 mol dm^{-3}) in $MeNO_2$. Reaction conditions: temperature 25 °C, $[H_2O_2]_0$ = 0.5 mol dm^{-3}, [catalyst] = 0.4×10^{-4} mol dm^{-3}, $[CH_3COOH]$ = 0.5 mol dm^{-3}. Concentrations were measured after addition of PPh_3.

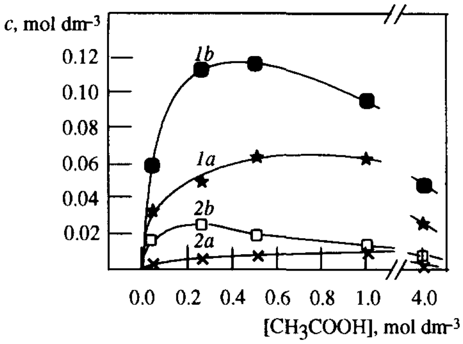


Figure 2. Dependences of concentrations of cyclohexanol (*1*) and cyclohexanone (*2*) formed in oxidation of cyclohexane (0.46 mol dm^{-3}) in MeCN on concentration of acetic acid added. Reaction conditions: temperature 20 °C, $[H_2O_2]_0 = 0.5$ mol dm^{-3}, [catalyst] = 0.4 × 10^{-4} mol dm^{-3}, time: 20 min (*a*), 2 h (*b*). Concentrations were measured after addition of PPh_3.

cyclohexanone) determined before treatment of the reaction sample with PPh_3 (Figure 4a) is much low than the concentration of the same products after reduction with PPh_3 (Figure 4b). This difference can be easily understood, if we assume either the partial decomposition of ROOH in GC to produce ring-opened products (e.g., adipic acid) or/and the appearance of ROOH as a separate peak on the chromatogram (in some cases we were able to detect such peaks).

Figure 5 shows the kinetic curves of the oxygenate accumulation at various catalyst concentrations. It can be concluded that the increase in the catalyst concentration gives rise to an increase in the initial rate of the oxidation and in the total yield of the products after 3 h, as well as to a noticeable decrease in the ratio cyclohexanol/cyclohexanone. Indeed, if at [1] = 0.3 × 10^{-4} mol dm^{-3} the ratio ol/one is approximately 10, at

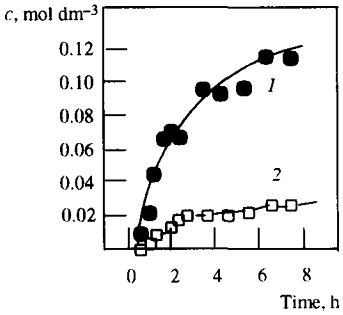


Figure 3. Kinetics of accumulation of cyclohexanol (*1*) and cyclohexanone (*2*) in the oxidation of cyclohexane (0.46 mol dm^{-3}) in MeCN. Reaction conditions: temperature 0 °C, $[H_2O_2]_0 = 0.5$ mol dm^{-3}, [catalyst] = 0.4 × 10^{-4} mol dm^{-3}, $[CH_3COOH] = 0.5$ mol dm^{-3}. Concentrations were measured after addition of PPh_3.

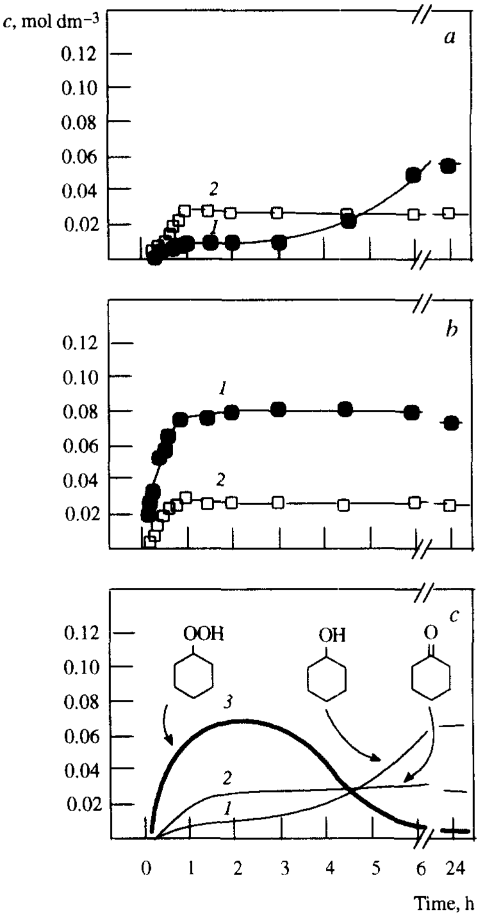


Figure 4. Kinetics of the accumulation of cyclohexanol (curves *1*), cyclohexanone (*2*) and cyclohexyl hydroperoxide (*3*) in the oxidation of cyclohexane (0.23 mol dm^{-3}) in MeCN. Reaction conditions: temperature 20 °C, $[H_2O_2]_0$ = 0.75 mol dm^{-3}, [catalyst] = 0.4×10^{-4} mol dm^{-3}, $[CH_3COOH]$ = 0.25 mol dm^{-3}. Concentrations were measured before (graph *a*) and after (graph *b*) addition of PPh_3. Real concentrations of products *1*, *2* and *3* (graph *c*) were calculated by comparison of the data presented on graphs *a* and *b*.

higher catalyst concentration (1.0×10^{-4} mol dm^{-3}) this value is only ~1.4. This difference can be due either to an enhanced amount of the ketone formed in ROOH decomposition (compare Figure 4) under the action of higher concentration of **1** or to the more efficient oxidation of the alcohol into ketone in the course of the reaction, when **1** is used in higher concentrations.

Table 1. Oxidation of normal higher alkanes [a]

	Ketones, $c \times 10^2$, mol dm^{-3}			Alcohols, $c \times 10^2$, mol dm^{-3}				
Substrate	-one-2	-one-3	one-4	-ol-1	-ol-2	-ol-3	-ol-4	C(1) : C(2) : C(3) : C(4) [b]
n-Pentane	1.4	0.6	–	0.26	2.7	1.2	–	1.0 : 15.7 : 14.0
n-Heptane	0.63	0.55	0.22	1.1	2.4	2.1	1.0	1.0 : 42.2 : 36.7 : 33.9

[a] Reaction conditions: solvent MeCN, temperature 20 °C, 2h, [substrate] = 0.23 mol dm^{-3}, $[H_2O_2]_0$ = 0.5 mol dm^{-3}, [catalyst] = 0.4 × 10^{-4} mol dm^{-3}, [CH_3COOH] = 0.5 mol dm^{-3}. Concentrations of the products were measured after addition of PPh_3.

[b] The relative normalized reactivities of the hydrogen atoms at carbon atoms 1, 2, 3, and 4 taking into account the number of hydrogen atoms at each of the carbon atoms.

Table 2. Oxidation of 2- and 3-methylpentane [a]

	Alcohols,[b] $c \times 10^2$, mol dm^{-3}			
Substrate	*primary*	*secondary*	*tertiary*	1° : 2° : 3° [c]
2-Methylpentane	0.20	1.7	4.5	1.0 : 19.1 : 204
3-Methylpentane	0.12	2.0	4.0	1.0 : 38.5 : 308

[a] Reaction conditions: see footnote to Table 1.

[b] Concentrations of isomeric alcohols only were used in calculations of bond selectivities.

[c] The relative normalized reactivities of hydrogen atoms at primary, secondary, and tertiary carbon atoms taking into account the number of hydrogen atoms at each of the carbon atoms.

In the oxidation of cyclohexane at [**1**] = 0.3 × 10^{-4} mol dm^{-3} at 20 °C after 2 h (Figure 5) the total concentration of the oxygenates is 0.1 mol dm^{-3}, and the turnover number attains 3300. The yield of the oxygenates after 2 h at [*cyclo*-C_6H_{12}]$_0$ = 0.23 mol dm^{-3} (Figure 4) is 46%, based on cyclohexane.

The data obtained from the present study on the oxidation of normal higher alkanes are summarized in Table 1. The regioselectivity in the oxidation of *n*-heptane is C(1) : C(2) : C(3) : C(4) ≈ 1 : 40 : 35 : 35, which is noticeably higher than the analogous parameter (~ 1 : 4 : 4 : 4) found in the oxidation by the system "O_2 – H_2O_2 – vanadate – pyrazine-2-carboxylic acid".[12] Since the latter reagent is believed to generate hydroxyl radicals as the active oxidation species, the Mn-catalyzed oxidation of alkanes does not seem to involve hydroxyl radicals.

In order to determine the bond selectivity in the reaction under discussion, we have carried out the oxidation of branched alkanes: 2-methylbutane, 2- and 3-methylpentanes and 3-methylhexane (Tables 2 and 3). The values of the bond selectivity 1° : 2° : 3° in these cases are in the region of 1 : (15–40) : (180–300). Again, this selectivity parameter is much higher than that established [11] for the oxidation of the methylhexane isomers by the hydroxyl-radical-generating systems 'O_2 – H_2O_2 – vanadate – pyrazine-2-carboxylic acid' [1 : (3–6) : (6–16)] and 'O_2 – H_2O_2 – hν' [1 : (4–5) : (15–20)].

Table 3. Oxidation of branched higher alkanes [a]

Substrate	Time, min	Sum of alcohols,[b] $c \times 10^2$, mol dm^{-3}	1° : 2° : 3° [c]
2-Methylbutane	5	0.5	1.0 : 12.3 : 172
	10	1.3	1.0 : 23.0 : 185
	30	3.3	1.0 : 25.0 : 208
	40	4.4	1.0 : 26.0 : 243
	60	4.9	1.0 : 27.0 : 288
3-Methylhexane	10	4.7	1.0 : 17.6 : 197
	20	6.9	1.0 : 14.8 : 169
	30	9.2	1.0 : 15.1 : 171
	45	11.3	1.0 : 15.9 : 183
	60	11.5	1.0 : 16.0 : 188
	90	12.3	1.0 : 16.2 : 192
	360	14.5	1.0 : 15.0 : 182

[a] Reaction conditions: see footnote to Table 1. [CH_3COOH] = 0.25 mol dm^{-3} in the case of 2-methylbutane and 0.5 mol dm^{-3} in the case of 3-methylhexane

[b] Concentrations of isomeric alcohols only were used in calculations of bond selectivities.

[c] The relative normalized reactivities of hydrogen atoms at primary, secondary, and tertiary carbon atoms taking into account the number of hydrogen atoms at each of the carbon atoms.

The oxidation of *cis*- and *trans*-decalin gives mixtures of various products. We analyzed only the alcohols (after treatment of the reaction solution with PPh_3) in which the hydroxyl groups substitute *tertiary* positions (Scheme 2). The data are summarized in Table 4. It is very interesting that *trans*-decalin is oxidized to produce almost exclusively *trans*-decal-9-ol, that is the reaction exhibits very high stereoselectivity (retention of configuration, RC_{trans} ~95%). Parameter RC_{trans} does not depend on the reaction time. However, the oxidation of *cis*-decalin, in which *tert*-C–H bonds are less sterically hindered, affords both *cis* and *trans* isomers of decal-9-ol, the ratio [*cis*]/[*trans*] being only around unity in the initial period of the reaction. After 10 min, this parameter reaches approximately 2 which remains constant during the reaction.

Table 4. Oxidation of decalin isomers [a]

	Oxidation of *cis*-decalin		Oxidation of *trans*-decalin	
Time	[*cis*]/[*trans*] [b]	RC_{cis} [c]	[*trans*]/[*cis*] [b]	RC_{trans} [d]
2 min	0.78	– [e]	– [f]	– [f]
5 min	1.06	3	~ 30	~ 95
10 min	2.33	40	~ 30	~ 95
15 min	2.12	36	~ 30	~ 95
30 min	2.19	37	~ 30	~ 95
4 h	2.14	36	~ 30	~ 95
20 h	2.14	36	~ 30	~ 95

[a] Reaction conditions: solvent MeCN, temperature 20 °C, [decalin] = 0.23 mol dm^{-3}, $[H_2O_2]_0$ = 0.2 mol dm^{-3}, [catalyst] = 0.4 × 10^{-4} mol dm^{-3}, [CH_3COOH] = 0.675 mol dm^{-3}. Concentrations of the products were measured after addition of PPh_3.

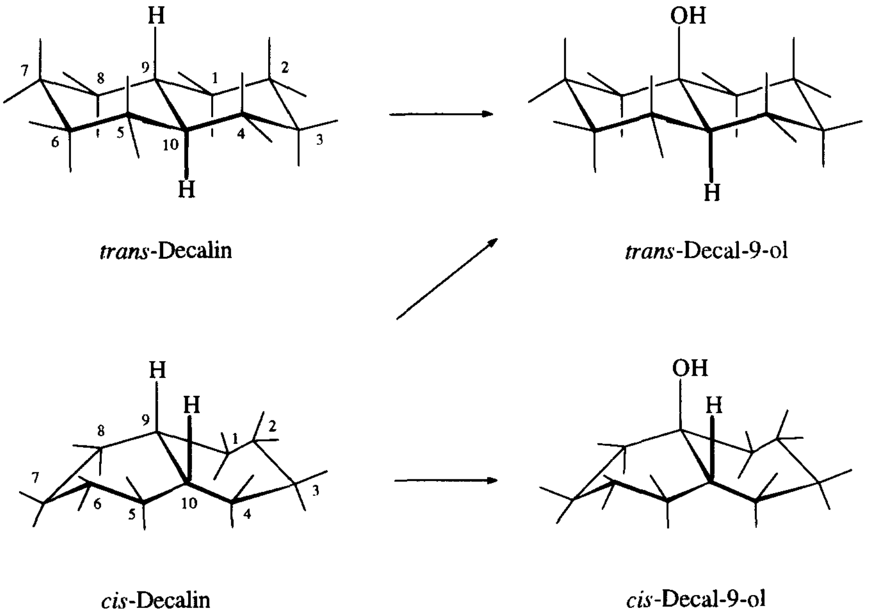
[b] The ratio of concentrations of *cis* to *trans* or *trans* to *cis* isomers of decal-9-ols (see Scheme 2).

[c] RC_{cis}= 100([*cis*] – [*trans*])/([*cis*] + [*trans*])%.

[d] RC_{trans}= 100([*trans*] – [*cis*])/([*trans*] + [*cis*])%.

[e] The value is negative.

[f] The concentrations of the products were too low to determine these parameters.



Scheme 2. Oxidation of isomeric decalins by the system "H_2O_2 – complex **1** – CH_3COOH" in acetonitrile (see Table 4).

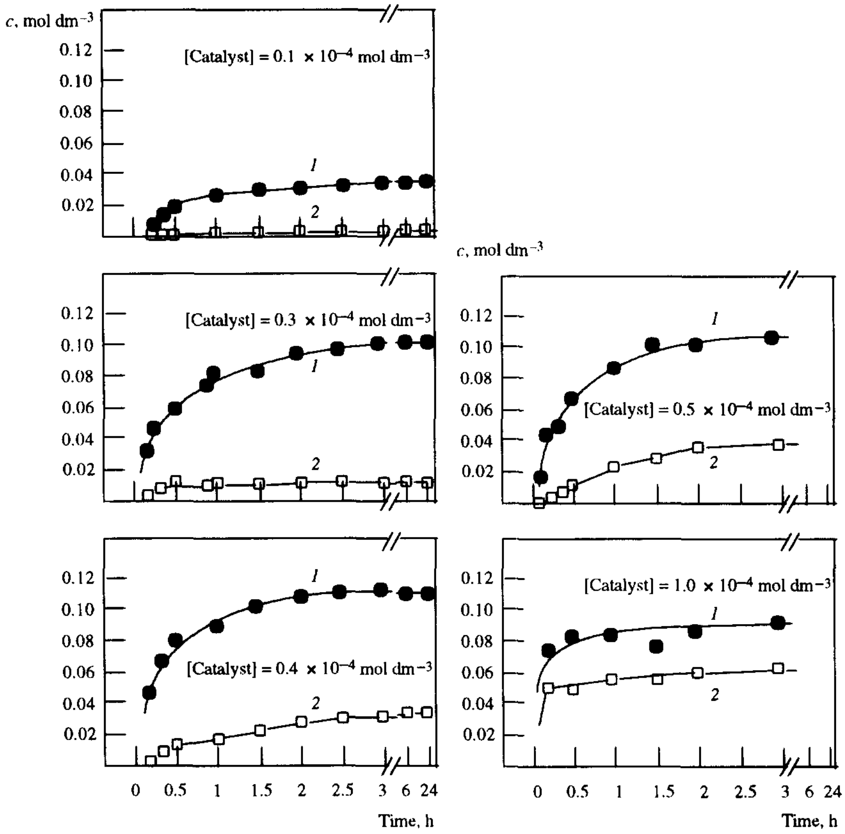


Figure 5. Kinetics of the cyclohexane (0.46 mol dm^{-3}) oxidation in MeCN at various catalyst concentrations. Reaction conditions: temperature 25 °C, $[H_2O_2]_0$ = 0.5 mol dm^{-3}, $[CH_3COOH]$ = 0.5 mol dm^{-3}. Concentrations of cyclohexanol (curves *1*) and cyclohexanone (*2*) were measured after addition of PPh_3.

Low values of RC_{cis} in the beginning of the oxidation testify that during the induction period the oxidation occurs via a different mechanism, possibly with participation of free radicals (e.g., $HO^{\bullet}$). It should be noted that in the oxidation of *cis*- and *trans*-decalin by "O_2 – H_2O_2 – vanadate – pyrazine-2-carboxylic acid" almost equal ratios [*trans*]/[*cis*] (84 : 16 for *cis*-decalin and 83 : 17 for *trans*-decalin), have been obtained independently of the starting isomer (*cis*- or *trans*-) of decalin.[11, 13]

It was very interesting to use the system described above in oxidations of lower alkanes. In the case of lower alkanes, oxidation processes usually occur at elevated (> 200 °C) temperatures, and light alkanes, which are the least reactive compounds among saturated hydrocarbons, are reacted not only at high temperature but also under high pressure.[14] Alkane activation by transition metal complexes in solution [1] allows to carry out various transformations with participation of C–H bonds under milder conditions. However, oxidations of light alkanes at temperatures below 100 °C have been described only in restricted number of publications (see, e.g., ref.[15]). Very recently, we demonstrated that soluble vanadium derivatives, when combined with pyrazine-2-carboxylic acid, catalyze the oxygenation [10,b,e,h,i; 11-13; 16a,b] (and also carboxylation [16c]) of light alkanes including methane with O_2/H_2O_2 in acetonitrile or water solution. This process which uses molecular oxygen as a true oxidant and hydrogen peroxide as a promoter (the latter provides hydroxyl radicals which abstract hydrogen atoms from alkane molecules) proceeds at temperature ≥ 25 °C.

Obviously, it is a very important problem to find systems that are capable of functionalizating light alkanes at room and even lower temperature, and this task becomes especially challenging taking into account that metal-containing enzymes convert light alkanes into oxygenates at ambient temperature and atmospheric pressure.[1a]

Table 5. Oxidation of propane under various conditions [a]

			Products (concentration, mol dm^{-3})					
Run	T, °C	Time, h	$CH_3CH(OOH)CH_3$	$CH_3CH(OH)CH_3$	CH_3COCH_3	$CH_3CH_2CH_2OOH$	$CH_3CH_2CH_2OH$	CH_3CH_2CHO
1 [b]	+27	3	0.060	0.006	0.020	0.046	0.0001	0.0015
2 [c]	+20	5	0.026	0.058	0.058	0.001	0.0036	0.0020
3 [c]	+20	36	0	0.050	0.109	0	0.0037	0.0010
4 [b]	0	21	0.039	0.039	0.042	0.001	0.0020	0.0010
5 [d]	0	21	0.052	0.038	0.063	0.001	0.0024	0.0022
6 [c]	0	36	0.001	0.040	0.106	0	0.0018	0.0009
7 [d,e]	0	2	0.023	0.003	0.020	0	0	0
8 [d,e]	0	21	0.020	0.020	0.043	0.001	0.0010	0.0010
9 [c]	−22	36	0.042	0.033	0.035	0.002	0.0021	0.0011

[a] Reaction conditions: solvent, MeCN; propane, 7 bar (at 20 °C); air, 1 bar (at 20 °C); $[H_2O_2]_0 = 0.5$ mol dm^{-3}; $[CH_3COOH] = 0.25$ mol dm^{-3}. Concentrations of the products were measured before and after addition of PPh_3. Value 0 means below detection limit 0. 5 × 10^{-4} mol dm^{-3}.
[b] [catalyst] = 0.4 × 10^{-4} mol dm^{-3}.
[c] [catalyst] = 2.0 × 10^{-4} mol dm^{-3}.
[d] [catalyst] = 1.0 × 10^{-4} mol dm^{-3}.
[e] Propane, 1 bar (at 20 °C); no air.

We have found that the oxidation of propane by the system under consideration gives rise to the formation of 2-hydroperoxypropane and acetone as the main products (Table 5). Other oxygenates are produced in less concentrations. It can be seen from Table 5 that during prolonged contact with the catalyst the peroxide decomposes to form the corresponding ketone and alcohol (compare runs 2 and 3, 7 and 8). Although the reaction at +20 °C is faster (total TON in run 3 is 818, the yield of oxygenates based on H_2O_2 is 33%) the yields of the products at 0 °C are approximately the same. In fact, at 0 °C TON attains 3100 (run 4) and the yield is

30% (run 6). It is important that even under atmospheric pressure at 0 °C the reaction proceeds efficiently (the yield 17% on H_2O_2 and 22% on propane in run 8). A linear dependence of the product concentrations on the initial hydrogen peroxide concentration has been found, when $[H_2O_2]_0 < 0.25$ mol dm^{-3}.

Normal butane and isobutane can be also very easily oxidized by the system under consideration. The results are presented in Table 6. The reaction with isobutane gives some amount of acetone which is probably formed via the decomposition of *t*-butyl hydroperoxide. Ethane and especially methane are less reactive in comparison with propane and butanes (Table 6).

Table 6. Oxidation of light alkanes [a]

Alkane (initial pressure at 20 °C, bar)	Products (concentration, mol dm^{-3})	TON [b]
Methane [c] (50)	CH_3OOH (0.0005), CH_3OH (0.005)	50 [c]
Ethane [c] (30)	CH_3CH_2OOH (0.017), CH_3CH_2OH (0.0067), CH_3CHO (0.013)	367 [c]
n-Butane (2)	$CH_3CH(OOH)CH_2CH_3$ (0.018) [c] (0.014) [d], $CH_3CH(OH)CH_2CH_3$ (0.062) [c] (0.023) [d], $CH_3COCH_2CH_3$ (0.072) [c] (0.051) [d], $CH_3CH_2CH_2CH_2OOH$ (0.001) [c] (0.001) [d], $CH_3CH_2CH_2CH_2OH$ (0.001) [c] (0.001) [d], $CH_3CH_2CH_2CHO$ (0.001) [c] (0.0001) [d]	1550 [c] 2250 [d]
iso-Butane (2)	$(CH_3)_3COOH$ (0.034) [c] (0.061) [d], $(CH_3)_3COH$ (0.66) [c] (0.017) [d], $(CH_3)_2CHCH_2OOH$ (0.0001) [c] (0.0018) [d], $(CH_3)_2CHCH_2OH$ (0.0008) [c] (0.0006) [d], $(CH_3)_2CHCHO$ (0.0011) [c] (0.0004) [d], CH_3COCH_3 (0.0015) [c] (0.005) [d]	1034 [c] 2145 [d]

[a] Reaction conditions: solvent, MeCN; air, 1 bar (at 20 °C); $[H_2O_2]_0 = 0.5$ mol dm^{-3}; $[CH_3COOH] = 0.25$ mol dm^{-3}. Concentrations of the products were measured before and after addition of PPh_3.

[b] Total turnover number

[c] [catalyst] = 1.0×10^{-4} mol dm^{-3}; 0 °C; 21 h.

[d] [catalyst] = 0.4×10^{-4} mol dm^{-3}; 27 °C; 3 h; no air.

We believe that the alkane oxidation catalyzed by complex **1** begins with the hydrogen atom abstraction from the alkane by an oxygen-centered radical or radical-like species. The active oxidant is probably a manganese complex, possibly an oxomanganese species, and reaction occurs in a cage or via an 'oxygen-rebound mechanism',[1a] both these routes would afford products with retention of stereochemistry. Further, alkyl radicals, $R^{\bullet}$, that escape from the solvent cage react with dioxygen to generate $ROO^{\bullet}$, and subsequently ROOH with some loss of stereochemistry. An alternative route, abstraction of the alkane H atom by a species Mn–$OO^{\bullet}$ to produce $R^{\bullet}$ and Mn–OOH, followed by the interaction of the two latter particles to give ROOH with retention of configuration cannot be excluded.

In conclusion, the metal-catalyzed oxidation of alkanes proceeding under very mild conditions which has been found in the present work opens new horizons for the saturated hydrocarbon processing. This system seems to be a competitor and possibly a model of the alkane oxidations catalyzed by metal-containing enzymes.

Experimental

The oxidations of higher hydrocarbons were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 10 cm^3. Initially, a portion of 30% aqueous solution of hydrogen peroxide ("Fluka") was added to the solution of the catalyst, substrate and acetic acid in acetonitrile ("Fluka", was distilled over P_2O_5 before the reaction).

The oxidation of light alkanes was carried out in an stainless steel autoclave with intensive stirring (volume of the reaction solution was 10 mL and total volume of autoclave was 100 mL). The autoclave was charged with air (under atmospheric pressure) and then, consecutively, with the reaction solution containing the catalyst and acetic acid in acetonitrile and the alkane to the appropriate pressure.

The reaction solutions were analyzed by GC (DANI-86.10, capillary column 50 m × 0.25 mm × 0.25 µm, Carbowax 20M; integrator SP-4400; the carrier gas was helium.). Each sample was analyzed twice, i.e. before and after the addition of the excess of solid PPh_3. Since alkyl hydroperoxides, which are transformed in the GC injector into a mixture of the corresponding ketone and alcohol, are quantitatively reduced with PPh_3 to give the corresponding alcohol, this method allows to calculate the real concentrations not only of the hydroperoxide but of the alcohols and ketones present in the solution at a given moment. Authentic samples of all oxygenated products were used to attribute the peaks in chromatograms (comparison of retention times was carried out for different regimes of GC-analysis). For quantitative analysis of the reaction products the internal calibration technique ($MeNO_2$ as the internal standard) was used.

Acknowledgements

This work was financially supported by the Swiss National Science Foundation (Grant 21-50430.97). G. B. Shul'pin thanks the University of Neuchâtel for the invitation for his stay during which part of this work was carried out. The authors are indebted to Mr. Vincent Ferrand, Mr. Laurent Plasseraud and Mrs. Sandrine Stanislas (Université de Neuchâtel, Switzerland) for help in this work.

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