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Oxidations by the reagent “O_2–H_2O_2–vanadium derivative–pyrazine-2-carboxylic acid”. Part 12. Main features, kinetics and mechanism of alkane hydroperoxidation

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Electronic Supplementary Information

Appendix 1. On the possibility of radical-chain oxygenation of alkanes

A very important question which arises is whether or not the radical-chain oxidation of the alkane with molecular oxygen is possible under our conditions. It is very useful to analyse the possibility of chain radical reaction for different alkanes having strong and weak C–H bonds at various temperatures. Here we will estimate the efficiency of initiated oxidation of some hydrocarbons *via* radical-chain mechanism which is widely accepted for liquid-phase oxidative transformations of saturated and alkylaromatic hydrocarbons.[2a,c, 8]

The mechanism of an initiated radical-chain process of liquid-phase oxidation of a hydrocarbon, RH, can be described by the following equations:

$$\mathrm{RH} \xrightarrow{W_\mathrm{i}} \mathrm{R}\bullet \qquad \textit{(chain initiation)} \qquad \text{(A1.1)}$$

$$\mathrm{R}\bullet + \mathrm{O_2} \longrightarrow \mathrm{ROO}\bullet \qquad \textit{(chain propagation)} \qquad \text{(A1.2)}$$

$$\mathrm{ROO}\bullet + \mathrm{RH} \xrightarrow{k_\mathrm{p}} \mathrm{ROOH} + \mathrm{R}\bullet \qquad \textit{(chain propagation)} \qquad \text{(A1.3)}$$

$$\mathrm{ROO}\bullet + \mathrm{ROO}\bullet \xrightarrow{k_\mathrm{t}} \text{nonradical products} \qquad \textit{(chain termination)} \qquad \text{(A1.4)}$$

In this scheme, R· are alkyl radicals, ROO· are peroxyl radicals, equation (A1.1) corresponds to the stage of radical generation with the rate W_i, equations (A1.2) and (A1.3) present the cycle of chain propagation, and reaction (A1.4) is the step of the chain termination. Let us assume that at low temperature the terminal product of the oxidation is alkyl hydroperoxide, ROOH. The following expression for the rate of alkyl hydroperoxide appearence, W_ROOH, corresponds to the above mechanism:

$$W_\mathrm{ROOH} = \frac{k_\mathrm{p}}{\sqrt{2k_\mathrm{t}}} \sqrt{W_\mathrm{i}}\,[\mathrm{RH}] \qquad \text{(A1.5)}$$

where k_p is the rate constant of the interaction between peroxyl radical and RH [reaction (A1.3)], and k_t is the rate constant of the chain termination [reaction (A1.4)]. The chain length of the process ν equals the ratio of the ROOH formation rate and the chain initiation rate:

$$\nu = \frac{W_{\mathrm{ROOH}}}{W_{\mathrm{i}}} \qquad \text{(A1.6)}$$

It follows from expression (A1.5) and (A1.6) that the rate W_{ROOH} increases and the chain length ν decreases with increasing W_{i}. The condition $W_{\mathrm{ROOH}} = W_{\mathrm{i}}$ evaluates the rate of RH oxidation, W^0_{ROOH}, *via* radical-chain mechanism with $\nu = 1$:

$$W^0_{\mathrm{ROOH}} = \left(\frac{k_{\mathrm{p}}}{\sqrt{2k_{\mathrm{t}}}}\right)^2 [\mathrm{RH}]^2 \qquad \text{(A1.7)}$$

At $W_{\mathrm{ROOH}} < W^0_{\mathrm{ROOH}}$ a radical-chain oxidation process is possible ($\nu > 1$), and at $W_{\mathrm{ROOH}} > W^0_{\mathrm{ROOH}}$ only the radical oxidation of RH with $\nu < 1$ is possible. Thus it may be stated that comparison of the effective rate of RH oxidation with the rate calculated using formula (A1.7) allows to make a conclusion about either a fundamental possibility or inability to associate the efficient process rate with the chain mechanism of the oxidation.

The value of W^0_{ROOH} is governed by so-called oxidizability parameter, $k_{\mathrm{p}}/\sqrt{2k_{\mathrm{t}}}$, and the hydrocarbon concentration. The values of oxidizability parameters are known for certain hydrocarbons, and can be calculated for others using values k_{p} and k_{t}. For methane and ethane oxidation in the liquid phase the rate constants for chain propagation, k_{p}, and chain termination, k_{t}, remain unknown. Therefore, any methods of estimation of these parameters, even quite approximate, are of considerable interest because they allow to get knowledge about the efficiency of the initiated radical-chain process of liquid-phase oxidation of the lower hydrocarbons. In order to evaluate the degree of accuracy in our estimations, analogous calculations have been carried out also for the hydrocarbons for which direct experimental data are known.

The rate constants for chain propagation, lg k_{p}, at 30 ºC and their dependences on temperature for certain hydrocarbons are collected in Table A1, Section (A). To estimate the rate constants k_{p} we used proposed previously[36a] empirical equation (A1.8):

$$\lg k_{\mathrm{p}} = -\mathrm{B} + 0.225\, D_{\mathrm{R\text{-}H}} + \frac{5900 - 98\, D_{\mathrm{R\text{-}H}}}{\mathrm{T}} \qquad \text{(A1.8)}$$

where the parameters are expressed: k_{p} in dm^3 mol^{-1} s^{-1}, $D_{\mathrm{R–H}}$ (*i.e.*, bond energy for the abstracted H atom) in kcal mol^{-1}, and B = –11.5 for hydrocarbons containing secondary C–H bonds and –12.5 for hydrocarbons with tertiary C–H bonds. For hydrocarbons having only primary C–H bonds, we accepted the value B = –11.5, that is equal to the parameter for hydrocarbons containing secondary C–H bonds. Using the same empirical equation (A1.8) we calculated the temperature dependence of k_{p} according to the relationships:

$$\lg A = -\mathrm{B} + 0.225\, D_{\mathrm{R–H}} \qquad (\mathrm{dm^3\ mol^{-1}\ s^{-1}}) \qquad \text{(A1.9)}$$

$$E = 4.575(5900 - 98\, D_{\mathrm{R–H}}) \times 10^{-3} \qquad (\mathrm{kcal\ mol^{-1}}) \qquad \text{(A1.10)}$$

Here A is preexponential factor for the rate constant and E is activation energy of the reaction. In our calculations we used either known from the literature value of bond energy in the hydrocarbon or this parameter was calculated previously according to equation (A1.8) using the k_{p} value at the fixed temperature.

Table A1, Section (B) summarizes the rate constants for chain termination (lg2k_{t}) and corresponding temperature dependences. In the cases when the temperature dependences are unknown the values of activation energy were accepted in accordance with the analysis of the literature data[36b] and for radicals $CH_3CH_2OO\cdot$ and $CH_3OO\cdot$ we used parameters determined for the gas-phase reactions. Section (C) collects also oxidizability parameters at 30 ºC,[2a, 36f] the same parameters extrapolated to 30 ºC and their temperature dependences according to the literature data,[36g] as well as these parameters calculated based on the arithmetical mean values given in Sections (A) and (B) of Table A1.

Table A1 Parameters for the liquid-phase H atom abstraction from the hydrocarbons, RH, by their peroxyl radicals, $ROO\cdot$ (A) and for termination reaction (B), as well as oxidizability parameters (C)

		(A) Reaction $RH + ROO\cdot \rightarrow R\cdot + ROOH$ [a]				(B) Reaction $ROO\cdot + ROO\cdot \rightarrow$ [a]			(C) Hydrocarbon oxidizability [b]	
No	Hydrocarbon, RH	lg k_p (30 ºC)/ $dm^3\ mol^{-1}\ s^{-1}$	lg A/ $dm^3\ mol^{-1}\ s^{-1}$	E/ kcal mol^{-1}	$D_{R–H}$/ kcal mol^{-1}	lg $2k_t$ (30 ºC)/ $dm^3\ mol^{-1}\ s^{-1}$	lg $2A_t$/ $dm^3\ mol^{-1}\ s^{-1}$	E_t, kcal mol^{-1}	lg ($k_p/\sqrt{2k_t}$) (30 ºC)/ $dm^{3/2}\ mol^{-½}\ s^{-½}$	E_{eff}/ kcal mol^{-1}
1	Tetralin	0.97 0.81 0.89[d]	5.58 4.9[c] 5.24[d]	6.4 5.7[c] 6.05[d]		6.82	9.93	4.3	–2.52	3.9
2	Cyclohexene	0.55 0.785 0.67[d]	5.6 4.9[c] 5.25[d]	7.0 5.7[c] 6.35[d]		6.45	10.8	6.0[g]	–2.56 –2.64[k] –2.60[d]	3.35
3	Ethylbenzene	–0.16 –0.2 –0.16 –0.17[d]	5.98 4.83 7.1[c] 6.0[d]	8.5 7.0 10.0[c] 8.5[d]		7.25	9.8	3.5[h]	–3.78 –3.68[k] –3.17[l] –3.54[d]	7.5 6.8[l] 7.15[d]
4	Toluene	–0.62 –0.17 –0.4[d]	8.1[c] 7.2[e] 7.65[d]	12.2[c] 10.2[e] 11.2[d]	83	8.48	9.86	2.0	–4.64 –5.0[k] –4.82[d]	10.2
5	Cumene	–0.77 –0.745 –0.76[d]	6.51 5.3[c] 5.9[d]	10.1 8.4[c] 9.2[d]		4.27	8.58	6.0	–2.89 –2.82[k] –2.83[l] –2.85[d]	6.25 6.8[l] 6.52[d]
6	Cyclohexane	–1.23[f]	9.6[f]	15.0[f]	94	6.5	11	6.0[i]	–4.48 –5.13[l] –4.80[d]	12.0 13.0[l] 12.5[d]
7	Ethane	–1.7	10.5	16.9	98	8.1[j]	8.4	0.5[j]	–5.75	16.9
8	Methane	–2.2	11.6	19.2	103	8.7[j]	8.1	–1[j]	–6.55	20

[a] Original data (from different publications) are taken from Ref. 36*b*. [b] The values of oxidizability parameter, $k_p/\sqrt{2k_t}$, and effective activation energy, $E_{eff} = E_p – ½E_t$, were calculated using data from Sections (A) and (B). [c] The temperature dependence of k_p has been calculated using k_p value at 30 ºC[36b] and equation (A1.6). [d] For some hydrocarbons, parameters lg k_p, lg A, E, lg ($k_p/\sqrt{2k_t}$) and E_{eff} are taken (or extrapolated) from different references, and in the last line arithmetical mean values calculated from upper values of the column are given. [e] The parameters were calculated according to equation (A1.8) using values for $D_{R–H}$ taken from Ref. 36*c*. [f] Calculated according to equation (A1.8) using lg k_p = –0.275 at 60 ºC[36c]. [g] Parameter for solution in CH_3OH (Ref. 32*b*). [h] Calculated based on data from Ref. 36*b*. [i] Parameter for solution in CH_3COOH (Ref. 36*b*). [j] Data for the reaction in the gas phase (Refs. 36*d*,*e*). [k] Data from Refs. 2*a*, 36*f*. [l] Data from Ref. 36*g*.

The table demonstrates that in the cases of hydrocarbons for which the experimental parameters are available, the estimated results are in tolerable agreement with the data obtained from direct measurements. Taking this into account, we believe that estimated by us values of parameter $k_p/\sqrt{2k_t}$ for ethane and methane can differ from the true values only by a factor of a few times. Using the arithmetical mean values from Table A1 (Section C) we calculated maximum possible rates of the RH oxidation, equal $2W^0_{ROOH}$, for the process occurring in accordance with the kinetic scheme (A1.1)–(A1.4) with the chain length equal to unity, as well as the minimum time of 10% RH conversion ($\tau_{0.1}$). The parameters W^0_{ROOH} were calculated according to equation (A1.7). The conversion time was determined by the integration of equation (A1.11):

$$-\frac{d[RH]}{dt} = 2\left(\frac{k_p}{\sqrt{2k_t}}\right)^2 [RH]^2 \qquad (A1.11)$$

which has been obtained for the kinetic scheme (A1.1)–(A1.4) under conditions

$$\nu = \frac{W_{ROOH}}{W_i} = 1 \qquad (A1.12)$$

and

$$2\frac{d[ROOH]}{dt} = -\frac{d[RH]}{dt} \qquad (A1.13)$$

This procedure gives the following expression for the 10% conversion time:

$$\tau_{0.1} = \frac{0.055}{[RH]_0 \left(\frac{k_p}{\sqrt{2k_t}}\right)^2} \qquad (A1.14)$$

Evidently, if $\nu > 1$ then $W_{ROOH} < W^0_{ROOH}$ and the $\tau_{0.1}$ value will be higher. Accepting [RH] = 1 mol dm^{-3} we will obtain the expressions for parameters W^0_{ROOH} and $\tau_{0.1}$. Both equations will contain only the oxidizability parameters. The results of such calculations are summarized in Table A2. It is follows from the data of this table that for a hydrocarbon such as cyclohexane and especially for much more inert ethane and methane at 30 ºC any really obtained rates will sufficiently exceed value of W^0_{ROOH}, that is, in principle, we have no reason to discuss the possibility of chain process according to scheme (A1.1)–(A1.4). Even at 100 ºC for the 10% transformation of ethane and methane via mechanism (24)–(27) the reactions will take 6.5 and 30 days, respectively, which testifies that the highest possible rate of the chain process is extremely low for these hydrocarbons. However, for hydrocarbons with weak C–H bonds, such as tetralin and cyclohexene (allylic methylenes), as well as cumene, corresponding transformations will take less than one hour and consequently are quite possible.

Table A2 Highest possible rates of the hydrocarbon chain-radical low-temperature oxidation (chain length $\nu = 1$ and $W^0_{ROOH} = W_i$) and the minimum possible times $\tau_{0.1}{}^0$ for the transformation of these hydrocarbons to the extent of 10% [a]

		Rate $W_{ROOH}{}^0$/mol dm^{-3} s^{-1}		Time $\tau_{0.1}{}^0$	
No	Hydrocarbon	30 ºC	100 ºC	30 ºC	100 ºC
1	Tetralin	9.1×10^{-6}	1.0×10^{-4}	1.7 hours	0.2 hours
2	Cyclohexene	6.3×10^{-6}	5.1×10^{-5}	2.5 hours	0.3 hours
3	Ethylbenzene	8.3×10^{-8}	7.3×10^{-6}	7.5 days	2.1 hours
4	Toluene	2.3×10^{-10}	1.0×10^{-7}	7.5 years	6.5 days
5	Cumene	2.0×10^{-6}	1.2×10^{-4}	7.5 hours	0.2 hours
6	Cyclohexane	5.5×10^{-11}	1.0×10^{-7}	32.5 years	6.5 days
7	Ethane	3.2×10^{-12}	1.0×10^{-7}	550 years	6.5 days
8	Methane	7.9×10^{-14}	2.1×10^{-8}	22000 years	30 days

[a] The parameters have been calculated in assumption of the hydrocarbon concentration of 1.0 mol dm^{-3} (which is lower in reality). Note that at $W_{ROOH} > W^0_{ROOH}$ the chain length $\nu < 1$ which corresponds to a non-chain process, and at $W_{ROOH} < W^0_{ROOH}$ parameter $\nu > 1$ and $\tau_{0.1} > \tau_{0.1}{}^0$.

Ions of transition metals could effectively interact with the alkyl hydroperoxide formed in the oxidation process even at relatively low temperature.[2*a*, 8, 36*b*] This interaction results in the peroxide decomposition to generate free radicals. In this case we have to add to the scheme (A1.1)–(A1.4) the following stages (M is an ion of transition metal in oxidized or reduced form):

$$\mathrm{ROOH} + \mathrm{M}(\mathit{ox}) \rightarrow \mathrm{ROO}\cdot + \mathrm{H}^+ + \mathrm{M}(\mathit{red}) \qquad \text{(A1.15)}$$

$$\mathrm{ROOH} + \mathrm{M}(\mathit{red}) \rightarrow \mathrm{RO}\cdot + \mathrm{HO}^- + \mathrm{M}(\mathit{ox}) \qquad \text{(A1.16)}$$

$$\mathrm{RO}\cdot + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R}\cdot \qquad \text{(A1.17)}$$

It should be noted that if in the case of mechanism (A1.1)–(A1.4) the final product of the reaction is alkyl hydroperoxide, ROOH, the mechanism (A1.15)–(A1.17), which is generated branching one, gives rise to the alcohol as a main product. The analysis of the kinetic scheme (A1.15)–(A1.17) gives expression (A.18) for the reaction rate.

$$W_{\mathrm{RH}} = \frac{3}{2}\left(\frac{k_{\mathrm{p}}}{\sqrt{2k_{\mathrm{t}}}}\right)^2 [\mathrm{RH}]^2 \qquad \text{(A1.18)}$$

Calculated to a constant coefficient, this equation coincides with equation (A1.7). Thus we can estimate the possibility of such a process determining the alcohol yield and analyzing the reaction products as well as comparing the data for the experimentally measured rate of this process with parameters from Table A2.

In our vanadium-catalysed oxidations, at least at low (< 50 ºC) temperatures and at least in the beginning of the reaction cyclohexane and normal alkanes are transformed only into alkyl hydroperoxides. Therefore, we can disregard a mechanism involving steps (A1.15)–(A1.17). Taking this into account, we conclude that, in accordance with data summarized in Table A2, the classical radical-chain mechanism (A1.1)–(A1.4) should be neglected for our case. However, this mechanism might be expected for easily oxidizable hydrocarbons such as tetralin, cyclohexene *etc*. It should be emphasized that our calculations do not exclude the possibility for the oxidation of cyclohexane, methane and other alkanes having strong C–H bonds with high rate *via* a radical non-chain mechanism where $W_{\mathrm{RH}} < W_{\mathrm{i}}$ ($\nu < 1$).

Appendix 2. Comparison with other alkane-oxygenating systems

The vanadium-based system described in the present work apparently has some mechanistic similarities with the “Fe(III) – Fe(II) – H_2O_2” system, as well as with Fenton's reagent (*i.e*., “Fe(II) – H_2O_2” system). The stoichiometric Fenton “Fe(II) – H_2O_2” system is transformed gradually into the catalytic “Fe(III) – Fe(II) – H_2O_2” system in the course of the hydrogen peroxide decomposition according to equation (47). Both systems operate in aqueous solution (see Refs. 8*b*, p. 118; 8*c*, p. 430; Refs. 19*a*, 37). The modified and complemented chain Haber–Weiss mechanism (Refs. 37*b*,*c* and 8b, p. 119) contains eleven stages (A2.1)–(A2.11):

$$\mathrm{Fe}^{3+} + \mathrm{H_2O} \rightleftharpoons \mathrm{Fe(OH)}^{2+} + \mathrm{H}^+ \qquad K = 2 \times 10^{-3}\ \mathrm{mol\ dm^{-3}} \qquad \text{(A2.1)}$$

$$\mathrm{Fe}^{3+} + \mathrm{H_2O_2} \rightleftharpoons \mathrm{Fe(OOH)}^{2+} + \mathrm{H}^+ \qquad K = 2 \times 10^{-3} \qquad \text{(A2.2)}$$

$$\mathrm{Fe(OOH)^{2+}} \rightarrow \mathrm{Fe^{2+}} + \mathrm{HOO\cdot} \qquad k = 1.6 \times 10^{-3}\ \mathrm{s^{-1}} \tag{A2.3}$$

$$\mathrm{Fe^{III}(OOH)^{2+}} + \mathrm{Fe^{III}(OH)^{2+}} \rightarrow$$

$$2\,\mathrm{Fe^{2+}} + \mathrm{H_2O} + \mathrm{O_2} \qquad k = 5.0\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{A2.4}$$

$$\mathrm{Fe^{2+}} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe^{3+}} + \mathrm{HO\cdot} + \mathrm{HO^-} \qquad k = 68\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{A2.5}$$

$$\mathrm{HO\cdot} + \mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \mathrm{HOO\cdot} \qquad k = 1.7 \times 10^{7}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{A2.6}$$

$$\mathrm{HOO\cdot} + \mathrm{Fe^{2+}} \rightarrow \mathrm{HOO^-} + \mathrm{Fe^{3+}} \qquad k = 2.1 \times 10^{6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{A2.7}$$

$$\mathrm{HOO\cdot} \rightleftharpoons \mathrm{H^+} + \mathrm{O_2\cdot^-} \qquad K = 1.3 \times 10^{-5}\ \mathrm{mol\ dm^{-3}} \tag{A2.8}$$

$$\mathrm{Fe^{3+}} + \mathrm{O_2\cdot^-} \rightarrow \mathrm{Fe^{2+}} + \mathrm{O_2} \qquad k = 4 \times 10^{8}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{A2.9}$$

$$\mathrm{Fe^{2+}} + \mathrm{HO\cdot} \rightarrow \mathrm{Fe^{3+}} + \mathrm{HO^-} \qquad k = 5.1 \times 10^{8}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{A2.10}$$

$$\mathrm{HOO\cdot} + \mathrm{HOO\cdot} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \qquad k = 2.4 \times 10^{6}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}} \tag{A2.11}$$

In this scheme for the decomposition of H_2O_2 to produce O_2 and H_2O, reactions (A2.3) and (A2.4) are the chain initiation steps, reactions (A2.5), (A2.6) and (A2.9) are the chain propagation steps and reactions (A2.7), (A2.10) and (A2.11) are the chain termination steps. Note that in the case (A2.1) concentration of H_2O is included into K. We realize that the mechanism proposed above for the alkane oxidation by "O_2 – H_2O_2 – n-Bu_4NVO_3 – PCA" reagent is a simplified one and possibly some reactions, for example, (A2.6) and (A2.11) can also operate in the V-catalysed oxidation. However, a good agreement between experimental data and parameters obtained from model calculations testifies that the model proposed for V-induced generation of hydroxyl radicals corresponds to the feasible mechanism of the alkane oxygenation. In general, the catalytic V-based system has many mechanistic similarities with the catalytic "Fe(III) – Fe(II) – H_2O_2" system, in both cases in the key step the interaction of H_2O_2 with low-valent form of metal complex affords hydroxyl radicals.

At high (> 60 ºC) temperatures in acetonitrile, the vanadium-based catalyst containing PCA decomposes hydrogen peroxide to produce O_2 and H_2O. This system is similar to the Fe(III) – Fe(II) combination. Thus in the case of V-catalysis the rising of the temperature enhances the catalase activity ($2H_2O_2 \rightarrow O_2 + 2H_2O$) at the expense of peroxidase activity. Although certain steps of V-catalysed hydrogen peroxide decomposition *via* the catalase route can be analogous to the steps presented in scheme (A2.1)–(A2.11), there are substantial differences. The main distinction is that reaction (A2.6) cannot be a predominant chain propagation step if acetonitrile is used as solvent and especially in the presence of cyclohexane. In both cases hydroxyl radicals will attack predominantly the solvent or the hydrocarbon. Indeed, the values for corresponding constants are $k_{25} = 3.5 \times 10^6$ (acetonitrile), $k_{24} = 3.0 \times 10^8$ (cyclohexane) and $k_{A2.6} = 1.7 \times 10^7$ (H_2O_2) $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$. Since the concentration of acetonitrile is approximately 30 times higher than that of hydrogen peroxide it means that the rate of interaction between $HO\cdot$ radicals and H_2O_2 is approximately 6 times lower than the rate of radical attack on acetonitrile.

The hydroxyl radical generation by the *catalytic* "O_2 – H_2O_2 – n-Bu_4NVO_3 – PCA" reagent is less efficient than that by the *stoichiometric* "Fe(II) – H_2O_2" system (Fenton's reagent). Indeed, the rate constant for reaction (A2.5) in water at 25 ºC (68 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$) is higher than the effective rate constant for the cyclohexane oxygenation with the V-reagent (0.44 $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ at 40 ºC). Let us compare, however, the activities of the peroxyl complex $Fe^{III}(OOH)^{2+}$ (equation A2.3) and the analogous vanadium(V) peroxy derivative $V(PCA)H_2O_2$ (equation 33) in monomolecular decomposition reactions to generate active species. The constant for the vanadium complex $k_{33} = 0.4\ \mathrm{s^{-1}}$ at 40 ºC and corresponding value for iron compound $k_{A2.3} = 1.6 \times 10^{-3}\ \mathrm{s^{-1}}$ at 25 ºC. Using the value $E_{A2.3}$ = 22 kcal mol^{-1} we can estimate $k_{A2.3} = 10^{-2}$ s^{-1} at 40 ºC. Thus it can be concluded that the activity of the vanadium complex with PCA in the generation of radicals in acetonitrile solution is more than one order of magnitude higher than that of ion Fe(III) in acidified aqueous solution.

The catalytic system "$Fe^{III}(ClO_4)_3 – H_2O_2$" in acetonitrile seems to be less efficient in comparison with the V-reagent (see Table 6). The recently described reagent "H_2O_2 – $[L_2Mn_2O_3](PF_6)_2$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) – MeCOOH"[16] oxidizes alkanes in acetonitrile with higher rates and turnover numbers (more than 3000 at room or even lower temperature). However, the mechanism of the latter system does not definitely involve the formation of hydroxyl radicals as reactive intermediates. Unlike the classical radical-chain oxidation of alkanes with molecular oxygen, the oxygenation with the V-reagent under discussion proceeds at relatively low temperature and gives rise to the formation mainly of alkyl hydroperoxides.

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