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Simple soluble Bi(III) salts as efficient catalysts for the oxidation of alkanes with $H_2O_2^{\dagger}$

Bruno G. M. Rocha,^a Maxim L. Kuznetsov,^{*a} Yuriy N. Kozlov,^b Armando J. L. Pombeiro^a and Georgiy B. Shul'pin*^b

Abstract

Simple catalytic system based on a soluble bismuth(III) salt Bi(NO₃)₃/H₂O₂/HNO₃/CH₃CN+H₂O exhibits pronounced activity towards the homogeneous oxidation of inert alkanes with the yield of oxygenate products up to 32 % and TON up to 112. The experimental selectivity parameters and kinetic data together with theoretical DFT calculations indicate that the reaction occurs via a free radical mechanism involving the formation of the HO[•] radicals which directly react with alkane molecules. The mechanism of the HO[•] generation (which is the rate limiting step of the whole process) includes the substitution of a water ligand for H₂O₂ in the initial aqua complex $[Bi(H_2O)_8]^{3+}$, hydrolysis of the coordinated H₂O₂, second H₂O-for-H₂O₂ substitution and the homolytic HO–OH bond cleavage in complex $[Bi(H_2O)_4(H_2O_2)(OOH)]^{2+}$ (6). The relatively low overall activation energy for this process (*ca.* 20 kcal/mol) is accounted for by the high lability and acidity of the Bi aqua complexes and tremendous activation of coordinated H₂O₂ in **6** towards homolysis.

Keywords: bismuth, hydrogen peroxide, alkanes, oxidation, DFT calculations, reaction mechanism, homogeneous catalysis, hydroxyl radical, water exchange.

^a Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisbon, Portugal. E-mail: max@mail.ist.utl.pt; Tel: +351 218419236

^b Semenov Institute of Chemical Physics, Russian Academy of Sciences, ulitsa Kosygina, dom 4, Moscow 119991 Russia. E-mails: Shulpin@chph.ras.ru, gbsh@mail.ru

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Introduction

Hydrocarbons are the most abundant carbon raw material and a search for their mild and efficient conversion to functionalized valuable products is an important problem of modern chemistry.¹ Such a transformation of alkanes as the most chemically inert hydrocarbons requires the presence of an appropriate oxidant and an efficient catalyst. Hydrogen peroxide is among the most promising oxidants from the ecological point of view. Oxidation reactions of alkanes with H_2O_2 are usually catalysed by various transition metal complexes (*e.g.* those of Fe, V, Mo, Mn, Ti, Os, Cu and others).¹ In contrast, the application of non-transition metal complexes in the homogeneous oxidation of simple alkanes containing non-activated C–H bonds with H_2O_2 is very little explored. The first work on this topic was previously published by some of us.² It was experimentally demonstrated that the simple catalytic system based on an aluminium salt, $Al(NO_3)_3/H_2O_2$, efficiently oxidizes alkanes in aqueous acetonitrile (total yield of oxygenate products up to 31 %). Other recently published preliminary experimental data revealed that the salts of such non-transition metals unconventional for the functionalization of alkanes as beryllium, zinc and cadmium $[M(NO_3)_2]$, also exhibit catalytic activity in the oxidation of cyclooctane with H_2O_2 .³

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Bismuth and its species are very little explored but promising non-transition metal catalysts for the hydrocarbon oxidation.⁴ Examples of the works on this topic include bismuth-catalysed allylic or benzylic oxidations with ¹BuOOH,⁵ benzylic oxidations by sodium bismuthate NaBiO₃ in acetic acid,⁶ the heterogeneous propylene and cyclohexane oxidations by molecular oxygen⁷ or $H_2O_2^{\ 8}$ catalysed by Bi-containing SBA-15, MCM-41, ZSM-5 mesoporous molecular sieves or the MoO_3 –Bi₂SiO₅/SiO₂ system, as well as the oxidation of propylene or isobutene to acrolein over the $Bi_xM_yO_z$ (M = Mo, W),⁹ Bi_{1-x/3}V_{1-x}Mo_xO₄¹⁰ or Bi₂Sn₂O₇¹¹ catalysts and epoxidation of stilbene by ¹BuOOH with [Cp₂Mo(Bi{OCH(CF₃)₂}₂)₂].¹² The interaction of bismuth oxide clusters with ethylene in the presence of O₂ was also theoretically studied.¹³

However, to our knowledge, there are no publications on the homogeneous oxidation of alkanes containing non-activated C-H bonds with H₂O₂ catalysed by Bi compounds. In this work,

we discovered that the simple soluble Bi salts can efficiently catalyse the oxidation of simple inert alkanes with hydrogen peroxide in aqueous acetonitrile solution. The detailed experimental study demonstrated that the reaction occurs via a Fenton-like mechanism including the formation of hydroxyl radicals which attack the C–H bonds of the alkane. The plausible mechanism of the HO[•] radicals generation in this system was investigated by theoretical methods.

Experimental section

Reagents. Salt Bi(NO₃)₃•5H₂O (98 %), hydrogen peroxide (50 % aqueous solution), cyclooctane (99.5 %), *n*-octane (99 %), methylcyclohexane (98 %), *trans-/cis*-dimethylcyclohexane (99 %) and HNO₃ (65 %) were used as received from Sigma-Aldrich.

Alkane oxidation. Catalyst was used as a stock solution prepared by simultaneous dissolving of Bi(NO₃)₃•5H₂O and HNO₃ (65 % aqueous) in acetonitrile. The reactions of alkanes were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring and using CH₃CN as solvent. Catalyst and co-catalyst (nitric acid) were introduced into the reaction mixture in the form of a stock solution in acetonitrile. Total volume of the reaction mixture was 10 mL. The substrate was then added and the reaction started when hydrogen peroxide was introduced in one portion. (CAUTION: the combination of air or molecular oxygen and H₂O₂ with organic compounds at elevated temperatures may be explosive!). The reactions were stopped by cooling and addition of excess of solid PPh₃. Solutions were analysed after addition of nitromethane as a standard compound by GC (instrument 'HP 5890 – Serie-II'; fused silica capillary columns column Hewlett-Packard; the stationary phase was polyethyleneglycol: INNOWAX with parameters 25 m × 0.2 mm × 0.4 µm; carrier gas was helium with column pressure of 15 psi) using the method developed previously by one of us.^{11,14} This method allows the estimate of concentrations of formed alkyl hydroperoxide, alcohol and ketone. Attribution of peaks was made by comparison with chromatograms of authentic samples.

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Computational details. The full geometry optimization of all structures and transition states (TS) has been carried out at the DFT/HF hybrid level of theory using Becke's three-parameter hybrid exchange functional in combination with the gradient-corrected correlation functional of Lee, Yang and Parr $(B3LYP)^{15}$ with the help of the Gaussian-09¹⁶ program package. The quasi-relativistic Stuttgart pseudopotential that described 78 core electrons (MWB78) and the appropriate contracted basis set¹⁷ were employed for the Bi atoms. This basis set was augmented by addition of the f-function with exponent 0.305 optimized using the utility gauopt for the Bi atom in the ground state. The standard basis set $6-311+G(d,p)^{18}$ was applied for all other atoms. No symmetry operations have been applied for any of the structures calculated. Restricted approximations for the structures with closed electron shells and unrestricted methods for the structures with open electron shells have been employed.

Taking into account the importance of the consideration of the second coordination sphere in the calculations of solvent effects for reactions involving highly charged species, one solvent molecule (H₂O or H₂O₂) was added explicitly in the second shell of the calculated structures. It was demonstrated in the previous works^{3,19,20} that the combination of the B3LYP functional, the basis sets used and the model with one explicit solvent molecule in the second coordination sphere provide an excellent agreement between the calculated and experimental activation energies of the water substitution reactions – two relevant steps of the calculated mechanism. Additionally, the O–O bond dissociation energy in H₂O₂ calculated at this level of theory (48.7 kcal/mol, the total gas-phase energy scale) is very close to the experimental value of 48.75 ± 0.005 kcal/mol.²¹

The Hessian matrix was calculated analytically for the optimized structures in order to prove the location of correct minima (no imaginary frequencies) or saddle points (only one imaginary frequency) and to estimate the thermodynamic parameters, the latter being calculated at 25 °C. The nature of all transition states was investigated by the analysis of vectors associated with the imaginary frequency and, in some cases, by the calculations of the intrinsic reaction coordinates (IRC) using the Gonzalez-Schlegel method.²²

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Total energies corrected for solvent effects (E_s) were estimated at the single-point calculations on the basis of gas-phase geometries using the polarizable continuum model in the CPCM version²³ with CH₃CN or, in some cases, H₂O as solvents. The calculations of the solvent effect were carried out using Gaussian-03²⁴ program package on the basis of gas-phase equilibrium structures found with Gaussian-09 to provide direct comparison of results obtained in this work and previously.^{3,19,20} The UAKS model was applied for the molecular cavity. The entropic term for the CH₃CN solvent (S_s) was calculated according to the procedure described by Wertz²⁵ and Cooper and Ziegler²⁶ using equations (C1) – (C4)

$$\Delta S_1 = R \ln(V_{m,liq}^s/V_{m,gas})$$
(C1)

$$\Delta S_2 = R \ln(V_{m,liq}^{\circ})$$
(C2)

$$\alpha = [S^{\circ,s}_{liq} - (S^{\circ,s}_{gas} + \Delta S_1)] / [S^{\circ,s}_{gas} + \Delta S_1]$$
(C3)

$$S_s = S_g + \Delta S_{sol} = S_g + [\Delta S_1 + \alpha (S_g + \Delta S_1) + \Delta S_2] =$$

$$S_g + [(-12.21 \text{ cal/mol} \cdot K) - 0.23(S_g - 12.21 \text{ cal/mol} \cdot K) + 5.87 \text{ cal/mol} \cdot K]$$
 (C4)

where $S_g = gas$ -phase entropy of solute, $\Delta S_{sol} = solvation entropy$, $S^{\circ,s}_{liq}$, $S^{\circ,s}_{gas}$ and $V^s_{m,liq} = standard entropies and molar volume of the solvent in liquid or gas phases (149.62 and 245.48 J/mol•K and 52.16 mL/mol, respectively, for CH₃CN), <math>V_{m,gas} = molar volume of the ideal gas at 25 °C (24450 mL/mol), V^{\circ}_m = molar volume of the solution corresponding to the standard conditions (1000 mL/mol). The S_s values for the H₂O solvent were calculated using the equation (C5).²⁶$

$$S_{s} = S_{g} + [(-14.3 \text{ cal/mol} \cdot K) - 0.46(S_{g} - 14.3 \text{ cal/mol} \cdot K) + 7.98 \text{ cal/mol} \cdot K]$$
(C5)

The enthalpies and Gibbs free energies in solution (H_s and G_s) were estimated using the expressions $H_s = E_s + H_g - E_g$ and $G_s = H_s - T \cdot S_s$, where E_g and H_g are the gas-phase total energy and enthalpy. The relative energies discussed in the text are Gibbs free energies in solution if not stated otherwise.

In the experimental study, the mixed solvent CH₃CN+H₂O was used. In calculations, the water part of this solvent was approximated by the explicit inclusion of one H₂O molecule in the

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second coordination shell, whereas the acetonitrile part of the solvent was approximated by the CPCM calculations of the bulky solvent effect for CH₃CN.

Results and Discussion

Main features of alkane oxidation catalysed by bismuth salts

For this study, the catalytic system Bi(NO₃)₃/H₂O₂/HNO₃/CH₃CN+H₂O was used. The catalyst was introduced in the form of nitrate Bi(NO₃)₃•5H₂O. Nitric acid was used to prevent the deep hydrolysis of the bismuth salt and formation of insoluble mono and polynuclear hydroxo- and oxo-complexes.

We have found that bismuth(III) nitrate catalyzes oxygenation of alkanes with hydrogen peroxide in acetonitrile if nitric acid is added in a small concentration to the reaction solution. Kinetic study of the cyclooctane oxidation was carried out by the GC method. The direct injection of a reaction sample into the chromatograph gave comparable amounts of cyclooctanol and cyclooctanone. An example of the experiments with direct injection is shown in Figure 1, graph A. The reduction of the sample with PPh₃ prior to the GC analysis lead to the exclusive formation of the alcohol, while no ketone is observed (Figure 1, graph B; see also Figures S7 and S8; for this method developed by Shul'pin, see Refs. 1i and 14). Such behaviour clearly indicates that cyclooctyl hydroperoxide ROOH is formed as the main primary product.^{1i,14} The formation of cyclooctyl hydroperoxide and its reduction to cyclooctanol with PPh₃ is shown in Scheme 1.

Figure 2 represents two examples of kinetic curves of oxygenate accumulation (mainly cyclooctyl hydroperoxide determined in the form of cyclooctanol after reduction with PPh₃) under various conditions. The maximum turnover number (TON) of 112 was attained under experimental conditions shown in Graph A, whereas Graph B demonstrates the experiment affording maximum yield 32 % based on initial cyclooctane. Yields of products under various conditions at different concentration of the bismuth salt are presented in Figures S1–S4.



Fig. 1 Accumulation of oxygenates with time in the cyclooctane (initial concentration 0.25 M) oxidation with H_2O_2 (1.2 M) catalysed by $Bi(NO_3)_3$ (1.0 × 10⁻³ M) in the presence of HNO₃ (0.072 M) in acetonitrile (contains H_2O_2 , 2.4 M) at 60 °C. Concentrations of cyclooctanol (-ol) and cyclooctanone (-one) were determined before (graph A) and after (graph B) reduction of the reaction samples with PPh₃.



Scheme 1 Oxidation of cyclooctane to cyclooctyl hydroperoxide and reduction of the latter with triphenylphosphine to cyclooctanol.

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Fig. 2 Accumulation of oxygenates (determined as cyclooctanol, curve 1, and cyclooctanone, curve 2, after reduction with PPh₃) with time in the cyclooctane (initial concentration 0.25 M) oxidation with H₂O₂ (1.2 M) catalysed by Bi(NO₃)₃ and HNO₃ (0.072 M) in acetonitrile (contains H₂O, 2.4 M). Graph A: $[Bi(NO_3)_3]_0 = 2.5 \times 10^{-4}$ M; at 60 °C. TON = 115; yield = 12 %. Graph B: $[Bi(NO_3)_3]_0 = 1.0 \times 10^{-3}$ M; at 75 °C TON = 80; yield = 32 %.

In special experiments, we studied the formation of oxygenates in the absence of the bismuth salt but in the presence of nitric acid and also in the absence of this co-catalyst (Figure 3). It can be seen that in the absence of Bi(NO₃)₃ the oxidation proceeds significantly less efficiently with the yield of oxygenates of less than 3 % after 32 hours *vs.* 21 % in the presence of Bi(NO₃)₃ under the same conditions (Figures 1B and 3). In the absence of both catalyst and co-catalyst (nitric acid), the reaction affords negligible concentrations of oxygenates (Figure 3, curves 1a and 2a). Dependence of the initial oxidation rate W_0 on the concentration of added HNO₃ in the "blank"

experiment is shown in Figure 4. The initial rate W_0 was determined from the slope of tangent to the

kinetic curve of total oxygenate accumulation (Figure 3, line 1b).



Fig. 3 "Blank" experiments in the absence of $Bi(NO_3)_3$. Accumulation of oxygenates (determined as cyclooctanol, curve 1 and cyclooctanone, curve 2 after reduction with PPh₃) with time in the cyclooctane (0.25 M) oxidation with H₂O₂ (1.2 M) in the presence of HNO₃ (0.072 M) in acetonitrile (contains H₂O, 2.4 M) at 60 °C. Analogous experiment in the absence of both Bi(NO₃)₃ and HNO₃ is presented by curves 1a and 2a. The tangent of kinetic curve 1 is shown by dotted straight line 1b.



Fig. 4 Dependence of initial reaction rate W_0 on concentration of nitric acid in the cyclooctane oxidation in the absence of Bi(NO₃)₃. Conditions: [cyclooctane]₀ = 0.25 M, [H₂O₂]₀ = 1.2 M (50% aqueous), solvent MeCN, 60 °C.

Using cyclooctane as a model substrate we studied dependences of the initial reaction rate W_0 (based on the sum of cyclohexanol and cyclohexanone concentrations measured after reduction of the reaction sample with PPh_3) on the initial concentration of each reactant at fixed concentrations of all other components of the reaction solution. These dependences are shown in Figures 5–8. The initial oxidation rate W_0 linearly depends on the initial concentration of Bi(NO₃)₃ (Figure 5), while the dependence on the concentration of added nitric acid is more complex (Figure 6). Such particular sigmoidal form of the latter trend may be accounted for by the hydrolysis processes. In the absence of HNO₃, the system is heterogeneous due to hydrolysis of the catalyst to the insoluble oxo and hydroxo mono and polynuclear species. The addition of a low amount of HNO_3 (ca. 0.2 M) is not sufficient to suppress the hydrolysis, and the catalyst is still inactive. Further addition of the acid results in an efficiently preventing of the hydrolysis and in homogenization of the system providing the rapid growth of the W₀ value. Finally, addition of HNO_3 at even higher concentrations leads to the saturation because the catalytic system is already homogeneous and hydrolysis is mostly suppressed. Additionally, due to a number of equilibria which exist in the reaction system (see below, Scheme 3) including pH-dependent equilibrium we have polyfactor influence of the acid presence. Note, that the hydrolysis and/or di- or even polymerization of the catalyst are inevitable, in some extent, even in the presence of a significant amount of HNO₃ due to the highly acid nature of Bi(III), and these processes should affect the TON values and yield of the products.

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The curve of dependence of W_0 vs. the initial concentration of cyclooctane approaches a plateau at $[RH]_0 > 0.2$ M as shown in Figure 7, curve 1. Addition of water decreases the initial reaction rate (Figure 8, curve 3). We carried out the Bi-catalysed oxidation of cyclooctane at different temperatures (Figure S5) what allowed the estimate of the effective activation energy of 20 ± 2.5 kcal mol⁻¹ (Figure 9).



Fig. 5 Dependence of the initial cyclooctane oxidation rate W_0 on the initial concentration of catalyst Bi(NO₃)₃ in the oxidation of cyclooctane (0.25 M) with H₂O₂ (1.2 M) in the presence of HNO₃ (0.072 M). Solvent MeCN, 60 °C.



Fig. 6 Dependence of the initial cyclooctane oxidation rate W_0 on the initial concentration of HNO₃ in the oxidation of cyclooctane (0.25 M) with H₂O₂ (1.2 M) catalysed by Bi(NO₃)₃ (1.0 × 10⁻³ M) in acetonitrile at 60 °C.

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Fig. 7 Curve 1: dependence of oxidation rate W_0 on initial concentration of cyclooctane (RH) in the oxidation of cyclooctane with H₂O₂ (1.2 M) in acetonitrile (contains H₂O, 2.4 M). Conditions: $[Bi(NO_3)_3]_0 = 1.0 \times 10^{-3}$ M; $[HNO_3]_0 = 0.072$ M; 60 °C. Concentrations of the products (cyclooctanol and cyclooctanone) were measured after reduction with PPh₃. Line 2: linearization of dependence presented by curve 1 using coordinates $[RH]_0 - [RH]_0/W_0$.

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Fig. 8 Curve 1: dependence of the initial cyclooctane oxidation rate W_0 on initial concentration of H₂O₂ in the oxidation of cyclooctane (0.25 M) catalysed by Bi(NO₃)₃ (1.0 × 10⁻³ M) in the presence of HNO₃ (0.007 M) in acetonitrile at 60 °C. Concentration of water [H₂O]_{total} was constant = 3.53 M. Curve 2: linearization of dependence presented by curve 1 using coordinates [H₂O₂]₀ – [H₂O₂]₀/ W_0 . Curve 3: dependence of W_0 on total concentration of water present in the reaction solution in the oxidation of cyclooctane (0.25 M) with H₂O₂ (1.2 M) catalysed by Bi(NO₃)₃ (1.0 × 10⁻³ M) in the presence of HNO₃ (0.007 M) in acetonitrile at 60 °C.



Fig. 9 The Arrhenius plot for the cyclooctane oxidation with H_2O_2 catalysed by complex Bi(NO₃)₃. Conditions: $[Bi(NO_3)_3]_0 = 1.0 \times 10^{-3}$ M; $[cyclooctane]_0 = 0.25$ M; $[H_2O_2]_0 = 1.2$ M; $[HNO_3]_0 = 0.072$ M) in acetonitrile (contains H₂O, 2.4 M). This dependence corresponds to the effective activation energy $E_a = 20 \pm 2.5$ kcal mol⁻¹. The original kinetic curves at different temperatures are presented in Figure S5.

A comparison of kinetic curves for the cyclooctane oxidations catalysed by bismuth and aluminum salts in the presence and absence of nitric acid is demonstrated in Figure S6. It can be seen that effect of addition of nitric acid is weaker in the case of aluminum in comparison with bismuth.

Selectivity of alkane oxidation

We measured the selectivity parameters of oxidations of certain linear and branched alkanes with H₂O₂ catalysed by the bismuth salt. These values coincide with the parameters determined previously for other systems based on vanadium, iron, osmium, nickel, rhenium and aluminium.^{2,27} These systems have been shown to oxidize alkanes with the formation of free hydroxyl radicals. Thus, the selectivity parameter in the *n*-octane oxidation (see Figure S7) is C(1) : C(2) : C(3) : C(4) = 1.0 : 4.4 : 4.3 : 4.0 (reactivities of the H atoms at carbons 1, 2, 3 and 4 of the *n*-octane chain

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which are relative normalized taking into account the number of hydrogen atoms at each carbon). The selectivity parameter in the oxidation of methylcyclohexane (see Figure S8) is $1^\circ : 2^\circ : 3^\circ = 1.0$: 4.2 : 16 (the relative normalized reactivities of hydrogen atoms at primary, secondary and tertiary carbons of methylcyclohexane). The oxidation of *cis*-1,2-dimethylcyclohexane and *trans*-1,2-dimethylcyclohexane proceeds non-stereoselectively (see Table 1 and Figure S9) with the *trans* : *cis* ratio being 0.7 : 0.8 (the ratio of isomers of *tert*-alcohols with mutual *trans*- and *cis*-orientation of the methyl groups formed in the oxidation of *cis*- and *trans*-1,2-dimethylcyclohexane).

	Content of products (%)						
Entry	Time (h)	trans-1,2-Dimethyl-1-hydroxycyclohexane	cis-1,2-Dimethyl-1-hydroxycyclohexane				
Oxidation of <i>cis</i> -1,2-dimethylcyclohexane							
1	1	42	58				
2	2	41	59				
3	3	39	61				
4	8	35	65				
Oxidation of <i>trans</i> -1,2-dimethylcyclohexane							
5	1	51	49				
6	2	43	57				
7	3	42	58				
8	8	38	62				

Table 1 Oxidation of *cis*- and *trans*-isomers of 1,2-dimethylcyclohexane^a

^{*a*} Reaction conditions: $[1,2\text{-dimethylcyclohexane}]_0 = 0.25 \text{ M}$, $[Bi(NO_3)_3]_0 = 1.0 \times 10^{-3} \text{ M}$; $[H_2O_2]_0 = 1.2 \text{ M}$; $[HNO_3]_0 = 0.072 \text{ M}$ in acetonitrile (contains H₂O, 2.4 M), 45 °C.

Kinetic analysis of cyclooctane oxidation

Selectivity parameters measured for the oxidation of linear and branched alkanes by the $Bi(NO_3)_3/H_2O_2/HNO_3/CH_3CN+H_2O$ system C(1) : C(2) : C(3) : C(4), $1^\circ : 2^\circ : 3^\circ$ and *trans* : *cis* indicate that the oxidation species operating in this system is hydroxyl radical (see previous section). Our kinetic data also support an assumption that hydroxyl radicals attack C–H bonds in saturated hydrocarbons. In the kinetic analysis described below we operate with the initial rate of

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the cyclooctyl hydroperoxide (ROOH) formation, $W_0 = (d[ROOH]/dt)_0$, which is equal to the initial rate of the oxygenate formation. This initial rate W_0 was determined from the slope of a dotted straight line which is tangent to the kinetic curve.

The mode of dependence of the alkane oxidation rate on its initial concentration (see Figure 7, curve 1) are in agreement with our second assumption about a competition between substrate (alkane) and solvent (acetonitrile) in the interaction with hydroxyl radicals generated by the system under consideration. It is reasonable to propose the simplest kinetic scheme which includes a stage of the radical generation (1) and two parallel stages of their consumption (2) and (3):

$$H_2O_2 \rightarrow \rightarrow HO^{\bullet}$$
 (1)

$$\mathrm{HO}^{\bullet} + \mathrm{RH} \to \to \mathrm{ROOH} \tag{2}$$

$$HO' + CH_3CN \rightarrow \text{products}$$
 (3)

Let us designate the hydroxyl radical generation rate in stage (1) as W_i . A detailed discussion of this parameter is given below. In the sequence of transformations of RH into ROOH, the rate-limiting step (with constant k_2) is the reaction between hydroxyl radical and the alkane leading to the formation of alkyl radical R^{*}. Reaction (3) with constant k_3 is a rate-limiting stage in the sequence of transformations (3) which affords products of acetonitrile oxidation. If we assume that concentration of hydroxyl radicals is quasi-stationary, analysis of the kinetic scheme (1)–(3), gives the following expression for the dependence of the ROOH accumulation rate on the concentration of cyclooctane, RH:

$$W_{0} = \left(\frac{d[\text{ROOH}]}{dt}\right)_{0} = \frac{k_{2}[\text{RH}]_{0}W_{i}}{k_{2}[\text{RH}]_{0} + k_{3}[\text{CH}_{3}\text{CN}]_{0}}$$
(4)

The following is the same dependence in more convenient form for the analysis form:

$$\frac{[\text{RH}]_0}{W_0} = \frac{1}{W_1} \left([\text{RH}]_0 + \frac{k_3}{k_2} [\text{CH}_3 \text{CN}]_0 \right)$$
(5)

Straight line 2 in Figure 7 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly testifies that the experimental dependence presented by curve 1 in this Figure 3 clearly depends on [RH]₀. For the conditions of experiments reflected by Figure 7, the following parameters of eq. (5) were calculated: k_3 [CH₃CN]₀/ $k_2 = 0.14$ M and $W_i = 6 \times 10^{-7}$ M s⁻¹. The first ratio characterizes the rates of interactions between hydroxyl radicals and acetonitrile and cyclooctane. The values of parameters k_3 [CH₃CN]/ $k_2 = 0.14$ M and $k_3/k_2 = 0.008$ (taking into account that [CH₃CN]₀ = 17 M) measured using the kinetic data presented in Figure 7 agree with the parameters expected for free hydroxyl radical. Indeed, these values for the catalytic systems which generate hydroxyl radicals have been reported to vary in the intervals k_3 [CH₃CN]/ $k_2 = 0.10-0.20$ M and $k_2/k_1 = 0.006-0.012$ (Table 2).

Entry	System	k_3 [CH ₃ CN]/ k_2 (M)	k_3/k_2	Ref.
1	H ₂ O ₂ /O ₂ /Bi(NO ₃) ₃ /HNO ₃	0.14	0.008	This work
2	H ₂ O ₂ /O ₂ /(<i>n</i> -Bu ₄ N)VO ₃ /PCA	0.14	0.008	28a
3	H ₂ O ₂ /O ₂ /"Cu ₄ "/CF ₃ COOH	0.20	0.012	28b
4	H ₂ O ₂ /O ₂ /" Cu ₄ "/HCl	0.10	0.006	28b
5	H ₂ O ₂ /O ₂ /[Co ₄ Fe ₂ OSae ₈]/HNO ₃	0.14	0.008	28c
6	H ₂ O ₂ /O ₂ /Cp* ₂ Os/py	0.09–0.19	0.0055-0.011	28d
7	H ₂ O ₂ /O ₂ /Cp ₂ Fe/Py/PCA	0.19	0.011	28e
8	H ₂ O ₂ /O ₂ /"Fe ₂ (TACN)"/PCA	0.19	0.011	27a

Table 2 Kinetic parameters for the oxidation of cyclohexane and acetonitrile with various systemsbased on $H_2O_2^a$

^{*a*} Abbreviations: PCA = pyrazine-2-carboxylic acid, "Cu₄" = tetracopper(II) triethanolaminate complex $[O \subset Cu_4 \{N(CH_2CH_2O)_3\}_4(BOH)_4][BF_4]_2$, $[Co_4Fe_2OSae_8] = complex$ $[Co_4Fe_2OSae_8] \cdot 4DMF \cdot H_2O$, where $H_2Sae = salicylidene-2$ -ethanolamine, $Cp*_2Os =$ decamethylosmocene, $Cp_2Fe =$ ferrocene, "Fe₂(TACN)" = an ironIII) complex with 1,4,7triazacyclononane. Concentration [CH₃CN] was assumed to be 17 M.

Experimentally found dependence of the cyclooctane oxidation rate W_0 on $[H_2O_2]_0$ (Figure 8) indicates the intermediate formation of an adduct A of the Bi species with hydrogen peroxide. Due to this, it is reasonable to add a stage of this complex formation (6) to the previously considered kinetic scheme (1)–(3):

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$$\text{``Bi'' + H_2O_2} \xrightarrow{K_6} A \tag{6}$$

Here "Bi" is the bismuth species introduced into the reaction mixture. Now we can say that the transformation (1) which affords hydroxyl radical is a monomolecular decay of the hydrogen peroxide complex A, and this decomposition is a rate-limiting stage:

$$A \rightarrow \rightarrow HO^{\bullet}$$
 (1a)

Let us assume that concentration [A] is quasi-stationary, that is $k_{-6} \gg k_1$, where k_{-6} is the rate constant of the reversed reaction in stage (6) and k_1 is the rate constant of the monomolecular transformation (1a) of A into hydroxyl radical with the rate W_i . Analysis of the sequence of transformations (6) and (1a) gives the following expression for the rate W_i taking into account that ["Bi"]₀ << [H₂O₂]₀:

$$W_{i} = \frac{k_{1}K_{6}["Bi"]_{0}[H_{2}O_{2}]}{1 + K_{6}[H_{2}O_{2}]}$$
(7)

Here ["Bi"]₀ is total concentration of the bismuth salt introduced into the solution and K_6 is equilibrium constant of transformation (6). Analysis of this equation demonstrates that at higher concentrations of H₂O₂ the rate W_i should not depend on the concentration of H₂O₂. Such a saturation was indeed observed experimentally (Figure 8).

Using eqs. (4) and (7) we obtain the expression for the alkane oxidation rate:

$$W_{0} = \left(\frac{d[\text{ROOH}]}{dt}\right)_{0} = \frac{k_{2}[\text{RH}]_{0}}{k_{2}[\text{RH}]_{0} + k_{3}[\text{CH}_{3}\text{CN}]_{0}} \times \frac{k_{1}[\text{"Bi"}]_{0}[\text{H}_{2}\text{O}_{2}]}{1 + K_{6}[\text{H}_{2}\text{O}_{2}]} = \Phi \times \frac{[\text{H}_{2}\text{O}_{2}]}{1 + K_{6}[\text{H}_{2}\text{O}_{2}]}$$
(8)

where

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$$\Phi = \frac{k_1 k_2 K_6 [\text{RH}]_0 [\text{"Bi"}]_0}{k_2 [\text{RH}]_0 + k_3 [\text{CH}_3 \text{CN}]_0}$$
(9)

Let us now transform eq. (8) into the form which is convenient for analysis of the experimental data:

$$\frac{[H_2O_2]}{W_0} = \frac{1}{\Phi} \left(1 + K_6[H_2O_2]\right)$$
(10)

Figure 8, line 2 testifies that the experimental dependence of W_0 on $[H_2O_2]$ shown by Figure 8, line 1 is described by eq. (10). In accordance with this equation we can calculate $K_6 = 1.3 \text{ M}^{-1}$ and $\Phi = 7.7 \times 10^{-7} \text{ s}^{-1}$. Inserting value Φ into eq. (9) using parameters $[RH]_0$, ["Bi"]₀ and $k_3[CH_3CN]/k_2 = 0.14$ M we can calculate $k_1 = 9 \times 10^{-4} \text{ s}^{-1}$ for the conditions of experiments shown in Figure 8.

Theoretical analysis of the catalytic system under discussion (see below) demonstrates that the most probable route of HO[•] radical generation is a monomolecular decay of a bismuth derivative containing two peroxide fragments. Due to this, we need to assume that the species denoted as "Bi" includes one peroxide molecule, and the following equilibrium exists:

$$Bi + H_2O_2 \quad \underbrace{K_{11}}_{\text{``Bi''}} \quad ``Bi'' \qquad (11)$$

The constant of equilibrium (11) is so high that under the conditions of our experiment shown in Figure 8 practically all bismuth is included into species "Bi". We can estimate this constant K_{11} if we accept the condition $K_{11}[H_2O_2] > 1$. Taking into account that in the experiment the minimum concentration of hydrogen peroxide is 0.1 M the value K_{11} should be higher than 10 M^{-1} and the second equilibrium constant of the diperoxo derivative formation $K_6 = 1.3 M^{-1}$ is noticeably lower that the first one K_{11} . This result obtained in the kinetic analysis of the experimental data is in good qualitative agreement with the result of the theoretical consideration of the system (see below).

Measuring the experimental effective activation energy for the catalytic system which includes bismuth salt we took into account that the cyclooctane oxidation proceeds in some extent also in the absence of the metal. The lower the temperature, the larger the contribution of the "blank" reaction W_{blank} to the total rate of the Bi-catalysed process W_{total} . Due to this, we determined the rate of the real Bi-catalysed reaction W_{cat} as the difference between the reaction rates measured in the presence and in the absence of bismuth salt: $W_{\text{cat}} = W_{\text{total}} - W_{\text{blank}}$. Since at temperature < 50 °C the rate of non-catalysed reaction is comparable with a half of the total observed oxidation rate, we analysed data obtained for temperature > 55 °C. The dependence of $\ln(W_{\text{cat}}) = \ln(W_{\text{total}} - W_{\text{blank}})$ on 1/T is presented in Figure 9. Analysis of this dependence leads to a value of the activation energy for the really Bi-catalysed reaction which is equal to 20 ± 2.5 kcal mol⁻¹.

Theoretical study of the reaction mechanism

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The experimental kinetic data and reaction selectivity parameters discussed above indicate that the Bi-catalysed oxidation of alkanes with H_2O_2 occurs via formation of highly reactive HO[•] radicals. The HO[•] radical then abstracts hydrogen from the alkane molecule to give alkyl radical R[•]. The latter reacts with molecular oxygen producing ROO[•] and then alkylhydroperoxide ROOH (Scheme 2). The mechanism of the HO[•] radical formation from H_2O_2 (the rate limiting step of the whole process) catalysed by transition metal complexes was initially proposed by Haber and Weiss²⁹ for the Fenton reagent, Fe(II) + H₂O₂. Since that time, it was revised in a number of works³⁰ and adapted later to the case of catalysts based on metals in the highest oxidation state. All these mechanisms include one-electron oxidation/reduction of the metal atom. However, their realization is more than questionable for the Bi(III) catalysts because the Bi(II) or Bi(IV) species are unstable and their formation is highly unfavourable.



Scheme 2 Radical mechanism of the Bi-catalysed alkanes oxidation with H₂O₂ (the rate limiting step of the whole process is boxed).

Recently, we applied theoretical methods for the elucidation of a plausible mechanism of the HO[•] generation from H₂O₂ catalysed by complexes of metals bearing a single stable non-zero oxidation state (Al, Ga, In, Sc, Y, La, Be, Zn, Cd).^{3,19,20} This mechanism includes (*i*) substitution of a water molecule for H₂O₂ in the aqua complexes $[M(H_2O)_n]^{k+}$ formed upon dissolution of corresponding nitrate M(NO₃)_k in aqueous CH₃CN, (*ii*) hydrolysis of the ligated hydrogen peroxide, (*iii*) substitution of other H₂O ligand for the second H₂O₂ molecule, (*iv*) elimination of a water ligand (in the case of Zn and Cd) and (*v*) monomolecular homolytic HO–OH bond cleavage in the key intermediate $[M(H_2O)_{(n-m)}(H_2O_2)(OOH)]^{(k-1)+}$ (Scheme 3).



Scheme 3 Mechanism of the HO' radical generation proposed for the systems $[M(H_2O)_n]^{k+}/H_2O_2$ (M = Al, Ga, In, Sc, Y, La, Be, Zn, Cd).

This mechanism does not require a change of the metal oxidation state. Instead, the OOH⁻ co-ligand in intermediate $[M(H_2O)_{n-m}(H_2O_2)(OOH)]^{(k-1)+}$ plays the same role as the transition metal does in the classical Fenton or Fenton-like processes, that is, the OOH⁻ ligand is easily oxidized by one electron upon the homolytic HO–OH bond cleavage leading to the stable complex $[M(H_2O)_{n-m}(OH)(^{\bullet}OOH)]^{(k-1)+}$. Here, we used theoretical DFT methods to investigate if the same mechanism may also be applied for the Bi catalyst, and results are discussed in the following sections.

(*i*) Initial catalytic form. Dissolution of bismuth nitrate in water in the presence of a strong acid results in the formation of aqua-complexes $[Bi(H_2O)_n]^{3+}$. The coordination number of Bi^{3+} in such solutions is highly variable, the formation of octa $(n = 8)^{31}$ or/and ennea $(n = 9)^{32}$ hydrates is

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usually proposed, while the structure $[Bi(H_2O)_9](SO_3CF_3)_3$ was determined by X-ray analysis for the triflate complex in solid state.³³

In order to estimate the relative stability of the octa- and enneahydrate forms of $[Bi(H_2O)_n]^{3+}$ within the theoretical model used in this work, the calculations of complexes $[Bi(H_2O)_9]^{3+}$ (1⁹), $[Bi(H_2O)_9](H_2O)^{3+}$ (1⁹-H₂O), $[Bi(H_2O)_8](H_2O)^{3+}$ (1⁸-H₂O) and $[Bi(H_2O)_8](H_2O)_2^{3+}$ (1⁸-2H₂O) were carried out. Both octahydrates were found to be slightly more stable than corresponding enneahydrates with the same number of H₂O molecules (by 1.4–2.0 kcal/mol in terms of ΔG_s , Table 3) what is in qualitative agreement with previous *ab initio* theoretical data.³⁴

Table 3 Calculated Gibbs free energies of activation (ΔG_s^{\neq}) and reaction (ΔG_s) in solution (in

KCal/III011	kcal/mol)	
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Reaction	$\Delta {G_s}^{\neq}$	$\Delta G_{\rm s}$
$[\mathrm{Bi}(\mathrm{H}_{2}\mathrm{O})_{9}]^{3^{+}}(1^{9}) \rightarrow [\mathrm{Bi}(\mathrm{H}_{2}\mathrm{O})_{8}](\mathrm{H}_{2}\mathrm{O})^{3^{+}}(1^{8}\mathbf{-H}_{2}\mathbf{O})$		-1.4
$[\operatorname{Bi}(\operatorname{H}_2\operatorname{O})_9](\operatorname{H}_2\operatorname{O})^{3^+}(1^9\operatorname{-}\mathbf{H}_2\operatorname{O}) \to [\operatorname{Bi}(\operatorname{H}_2\operatorname{O})_8](\operatorname{H}_2\operatorname{O})_2^{3^+}(1^8\operatorname{-}2\mathbf{H}_2\operatorname{O})$		-2.0
$[Bi(H_2O)_8](H_2O_2)^{3+} (\mathbf{1^{8}-H_2O_2}) \rightarrow [Bi(H_2O)_7](H_2O)(H_2O_2)^{3+} (\mathbf{2^7-H_2O-H_2O_2}) $ via TS1	5.8	1.2
$[\text{Bi}(\text{H}_2\text{O})_7](\text{H}_2\text{O})(\text{H}_2\text{O}_2)^{3+} (2^7 - \mathbf{H}_2\text{O} - \mathbf{H}_2\text{O}_2) \rightarrow [\text{Bi}(\text{H}_2\text{O})_7(\text{H}_2\text{O}_2)](\text{H}_2\text{O})^{3+} (3^8 - \mathbf{H}_2\text{O}) \text{ via } \mathbf{TS2}$	4.3	-0.4
$[\text{Bi}(\text{H}_2\text{O})_7(\text{H}_2\text{O}_2)](\text{H}_2\text{O})^{3^+}(\mathbf{3^8}\text{-}\mathbf{H}_2\text{O}) \rightarrow [\text{Bi}(\text{H}_2\text{O})_5(\text{OOH})](\text{H}_2\text{O})^{2^+}(\mathbf{4^6}\text{-}\mathbf{H}_2\text{O}) + \text{H}_3\text{O}^+ + \text{H}_2\text{O})$		2.6
$[\mathrm{Bi}(\mathrm{H}_{2}\mathrm{O})_{5}(\mathrm{OOH})](\mathrm{H}_{2}\mathrm{O})^{2^{+}}(4^{6}\mathbf{-H}_{2}\mathbf{O}) + \mathrm{H}_{2}\mathrm{O}_{2} \rightarrow$		
$[Bi(H_2O)_4(OOH)](H_2O)(H_2O_2)^{2+} (5^5 - H_2O - H_2O_2) + H_2O $ via TS3	9.8	7.9
$[\mathrm{Bi}(\mathrm{H}_{2}\mathrm{O})_{4}(\mathrm{OOH})](\mathrm{H}_{2}\mathrm{O})(\mathrm{H}_{2}\mathrm{O}_{2})^{2^{+}}(5^{5}\mathbf{-H}_{2}\mathbf{O}\mathbf{-H}_{2}\mathbf{O}_{2}) \rightarrow$	3.0	-1.5
$[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2+} (6^6-H_2O) $ via TS4		
$[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2+} (6^6 - H_2O) \rightarrow [Bi(H_2O)_4(OH)(OOH)](H_2O)^{2+*} (7^6 - H_2Oa) + HO^*$		5.5
$[\mathrm{Bi}(\mathrm{H}_{2}\mathrm{O})_{4}(\mathrm{OH})(\mathrm{OOH})](\mathrm{H}_{2}\mathrm{O})^{2+\star}(7^{6}-\mathbf{H}_{2}\mathbf{Oa}) \rightarrow [\mathrm{Bi}(\mathrm{H}_{2}\mathrm{O})_{4}(\mathrm{OH})(\mathrm{OOH})](\mathrm{H}_{2}\mathrm{O})^{2+\star}(7^{6}-\mathbf{H}_{2}\mathbf{Ob})$		-1.8
$[Bi^{III}(H_2O)_7(H_2O_2)](H_2O)^{3+} (3^8 - H_2O) \rightarrow [Bi^{IV}(H_2O)_7(OH)](H_2O)^{3+} + HO^{\bullet}$		39.8
$[\mathrm{Bi}^{\mathrm{III}}(\mathrm{H}_{2}\mathrm{O})_{5}(\mathrm{OOH})](\mathrm{H}_{2}\mathrm{O})^{2^{+}}(\mathbf{4^{6}-H}_{2}\mathbf{O}) \rightarrow [\mathrm{Bi}^{\mathrm{III}}(\mathrm{H}_{2}\mathrm{O})_{5}](\mathrm{H}_{2}\mathrm{O})^{2^{+}} + \mathrm{HOO^{*}}$		37.5
$[\mathrm{Bi}^{\mathrm{III}}(\mathrm{H}_{2}\mathrm{O})_{4}(\mathrm{H}_{2}\mathrm{O}_{2})(\mathrm{OOH})](\mathrm{H}_{2}\mathrm{O})^{2^{+}}(6^{6}\mathbf{-H}_{2}\mathbf{O}) \rightarrow [\mathrm{Bi}^{\mathrm{II}}(\mathrm{H}_{2}\mathrm{O})_{4}(\mathrm{H}_{2}\mathrm{O}_{2})](\mathrm{H}_{2}\mathrm{O})^{2^{+}} + \mathrm{HOO}^{\bullet}$		35.9
$[\operatorname{Bi}(\operatorname{H_2O})_5(\operatorname{OOH})](\operatorname{H_2O})^{2^+}(\mathbf{4^6}\text{-}\mathbf{H_2O}) \to [\operatorname{Bi}(\operatorname{H_2O})_5(\operatorname{O})](\operatorname{H_2O})^{2^+} + \operatorname{HO}^{\bullet}$		38.5
$[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2+} (6^6 - H_2O) \rightarrow [Bi(H_2O)_4(H_2O_2)(O)](H_2O)^{2+} + HO^{\bullet}$		37.7
$H_2O_2 \rightarrow 2HO'$		39.4
$[\text{Bi}(\text{H}_2\text{O})_7(\text{H}_2\text{O}_2)](\text{H}_2\text{O})^{3^+}(\boldsymbol{3^8}\text{-}\boldsymbol{H}_2\text{O}) \rightarrow [\text{Bi}(\text{H}_2\text{O})_3(\text{OH})_3](\text{H}_2\text{O})^{2^+}(\boldsymbol{9}) + \text{H}_3\text{O}^+ + 2\text{H}_2\text{O}$		24.1

The calculated structures of complexes 1^9 and 1^8 correspond to the tricapped trigonal prismatic and square antiprismatic polyhedra without noticeable distortions demonstrating no

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stereochemical influence of the Bi lone electron pair (Figure 10*i* and *ii*). The calculated mean Bi–O bond length in **1⁸-2H₂O** (2.48 Å) is in reasonable agreement with experimental EXAFS and LAXS solution data for the octa-coordinated Bi(III) ion (2.41(1) Å).³¹



Fig. 10 Idealized polyhedra of some calculated structures.

(*ii*) First H_2O -for- H_2O_2 substitution. At the first step of the investigated mechanism, one of the water ligands in $[Bi(H_2O)_n]^{3+}$ is substituted for the H_2O_2 molecule. The water exchange process is known for aqua-complexes of the most of metals.³⁵ Apparently, in the presence of a significant amount of H_2O_2 , the similar substitution of coordinated H_2O for H_2O_2 should occur.

For this step, only a mechanism of the dissociative type D was found. It includes the elimination of one water ligand from $[Bi(H_2O)_8](H_2O_2)^{3+}$ 1⁸-H₂O₂ to the second coordination sphere and the formation of intermediate $[Bi(H_2O)_7](H_2O)(H_2O_2)^{3+}$ (2⁷-H₂O-H₂O₂) with a reduced coordination number of Bi via TS1 (Scheme 4). This intermediate is then transformed into the hydrogen peroxide adduct $[Bi(H_2O)_7(H_2O_2)](H_2O)^{3+}$ (3⁸-H₂O) via TS2 upon coordination of H₂O₂ to the metal. The coordination polyhedron of 2⁷-H₂O-H₂O₂ is capped trigonal prism (Figure 10*iii*), whereas that of 3⁸-H₂O is distorted square antiprism (Figure 10*ii*). Both these complexes are only slightly endoergonic relative to the starting 1⁸-H₂O₂ (by 1.2 and 0.9 kcal/mol, respectively) reflecting very flexible coordination sphere of Bi. The Bi–O₂H₂ bond in 3⁸-H₂O (2.606 Å) is longer than the Bi–OH₂ bonds by 0.11–0.15 Å demonstrating a weaker binding of hydrogen peroxide to the metal in comparison with water. The energies of TS1 and TS2 are very similar, the former

being less stable only by 0.3 kcal/mol (Figure 11). The activation barrier of the water substitution is 5.8 kcal/mol (Table 3). Such a low value indicates a high lability of the bismuth aqua-complexes that correlates with the water-exchange rate for Bi(III) of $\sim 5 \times 10^6$ s⁻¹ (Ref. 36) comparable with In³⁺ (Ref. 37). Thus, the formation of the hydrogen peroxide adduct **3⁸-H₂O** in solution is favourable in terms of both kinetic and thermodynamic arguments.



Scheme 4 Mechanism of the H_2O -for- H_2O_2 substitution in $[Bi(H_2O)_8]^{3+}$ (second-sphere solvent molecules are omitted).

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All attempts to located a nona-coordinated intermediate $[Bi(H_2O)_8(H_2O_2)]^{3+}$ of the associative mechanism A or transition state of the concerted (interchange) mechanisms I, I_a or I_d failed and, therefore, the realization of these mechanisms may be ruled out.

(*iii*) Hydrolysis of the hydrogen peroxide adduct. It is well known that Bi(III) in aqueous solution is a strong acid with pK_a value of 1.1 (Ref. 38) and it undergoes an intensive hydrolysis. At the first step of the hydrolysis, the H⁺ abstraction from a protic ligand by an outer-sphere water molecule occurs. Taking into account the more acidic nature of H₂O₂ compared to H₂O, the former ligand should preferentially undergo such a deprotonation in $[Bi(H_2O)_7(H_2O_2)](H_2O)^{3+}$ **3⁸-H₂O** leading to the formation of the hydroperoxo species $[Bi(H_2O)_m(OOH)]^{2+}$ (Scheme 5). In neutral or weakly acidic media, the hydrolysis goes further and leads to the formation of various mono and polynuclear hydroxo- and oxo-complexes many of them being insoluble.³⁹ However, in strongly acidic media the hydrolysis is expected to be mostly restricted by its first step, *i.e.* deprotonation of H₂O₂ in **3⁸-H₂O**.



Scheme 5 Hydrolysis of coordinated hydrogen peroxide in $[Bi(H_2O)_7(H_2O_2)]^{3+}$ (second-sphere solvent molecules are omitted).



Fig. 11 General energy profile for the proposed mechanism of the HO[•] generation (only metalcontaining species and the HO[•] radical are indicated, second-sphere solvent molecules are omitted, numbers indicate the relative energies).

The geometry optimization of the octa-coordinated hydrolytic product $[Bi(H_2O)_7(OOH)](H_2O)^{2+}$ was undertaken. However, all attempts resulted in an extrusion of two water molecules from the first coordination sphere. As a result, the equilibrium structure of the hexa-coordinated complex $[Bi(H_2O)_5(OOH)](H_2O)^{2+}$ (4⁶-H₂O) was obtained. The coordination polyhedron of 4⁶-H₂O is a highly distorted pentagonal pyramid with the OOH⁻ ligand being in the axial position (Figure 10*iv*). Such a structure reflects a well-known effect of the stereochemically active lone electron pair of Bi, and the similar structural motif was found in solid state for various Bi complexes.⁴⁰

The CPCM method and the model used in this work do not allow accurate estimates of the ΔG_s value of hydrolysis of $\mathbf{3^{8}}^{.19}$ Hence, this value was calculated using the experimental pK_a value of Bi(III) (1.1 [Ref. 38]) and the corresponding thermodynamic cycle (see ESI for details). Thus calculated ΔG_s of hydrolysis of $\mathbf{3^8}$ is only 2.6 kcal/mol demonstrating that the H₂O₂ ligand in $\mathbf{3^8}$ -**H₂O** is highly acidic. At the same time, it is curious that the ΔG_s values of H₂O₂ hydrolysis in the aqua-complexes [M(H₂O)₅(H₂O₂)]³⁺ (M = Al, Ga, In) are even lower than that for Bi (0.6–2.2 kcal/mol),^{19,20} that is, the H₂O₂ ligand in the complexes of Al, Ga and In is even more acidic.

(*iv*) Second H₂O-for-H₂O₂ substitution. At the next step of the proposed mechanism, the substitution of another H₂O ligand for H₂O₂ occurs. For this step, the dissociative mechanism D is also realized and it includes dissociation of a water ligand from $[Bi(H_2O)_5(OOH)](H_2O_2)^{2+} 4^6$ -H₂O₂, via TS3, to give complex $[Bi(H_2O)_4(OOH)](H_2O)(H_2O_2)^{2+} (5^5-H_2O-H_2O_2)$ followed by the coordination of H₂O₂ to Bi and formation of $[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2+} (6^6-H_2O)$ via TS4 (Scheme 6). The coordination polyhedron of 6^6 -H₂O is also a distorted pentagonal pyramid, while that of 5^5 -H₂O-H₂O₂ is a highly distorted square pyramid (Figure 10*v*). In both cases, the OOH⁻ ligand occupies the axial position. The square pyramidal structural motif is also known for Bi(III) species.^{40a,41} Both intermediate 5^5 -H₂O-H₂O₂ and complex 6^6 -H₂O are noticeably endoergonic relative to 4^6 -H₂O (by 7.9 and 6.4 kcal/mol, respectively, Table 3). The activation barrier of the second water substitution step is 10.9 kcal/mol and this is noticeably higher than that of the first substitution (5.8 kcal/mol, Table 3).



Scheme 6 Mechanism of the second H_2O -for- H_2O_2 substitution (second-sphere solvent molecules

(*v*) Formation of HO' radicals. Theoretical studies of the discussed mechanism for the catalytic systems based on the aqua-complexes of the Group III metals $[M(H_2O)_n]^{3^+}$ (M = Al, Ga, In, Sc, Y, La) indicated that the hydrogen peroxide ligand in intermediates $[M(H_2O)_{n-2}(H_2O_2)(OOH)]^{2^+}$ is highly activated towards the homolytic HO–OH bond cleavage.^{19,20} Careful analysis and scan of the potential energy surface revealed that the HO' generation upon homolytic HO–OH bond rupture in $[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2^+}$ 6⁶-H₂O results in the formation of complex $[Bi(H_2O)_4(OH)(OOH)](H_2O)^{2^{++}}$ (7⁶-H₂Oa) (Scheme 7) and this process requires only 5.5 kcal/mol (*vs.* 39.4 kcal/mol in free H₂O₂, Table 3). This value is quite comparable with the calculated adiabatic HO–OH bond energies in $[M(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2^+}$ for M = Al, Ga, In and Sc (4.4–7.5 kcal/mol).^{19,20} Thus, the ability of Bi(III) to activate hydrogen peroxide towards the HO' formation is similar to that of the non-transition metals of the Group III. The formed complex $[Bi(H_2O)_4(OH)(OOH)](H_2O)^{2^{++}}$ (7⁶-H₂Oa) is then transformed to another isomer 7⁶-H₂Ob with the energy lower by 1.8 kcal/mol than 7⁶-H₂Oa.

The principal reasons of such tremendous activation of H_2O_2 in $[M(H_2O)_4(H_2O_2)(OOH)]^{2+}$ are (*i*) ability of the OOH⁻ ligand in the product $[M(H_2O)_4(OH)(OOH)]^{2+*}$ to be easily oxidized to HOO^{*} (Scheme 7) and (*ii*) delocalization of the spin electron density among two oxygen atoms of the OOH ligand in the product $[M(H_2O)_4(OH)(OOH)]^{2+*}$ (Figure 12).^{19,20} Note that the oxidation state of Bi(III) is not changed upon the reaction 6^6 - $H_2O \rightarrow 7^6$ - H_2O . Instead, the oxidation of the OOH⁻ co-ligand stabilizes the product of the HO–OH bond cleavage 7^6 - H_2O and, hence, activates H_2O_2 towards its decomposition.

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Scheme 7 HO–OH bond cleavage in $[Bi(H_2O)_4(H_2O_2)(OOH)]^{2+}$ (valence electrons and oxidation states of the oxygen atoms are shown).



Fig. 12 Spin density distribution in 7^6 -H₂O.

It is important that the ΔG_s energies required for the formation of the HO' or HOO' radicals accompanied by the one-electron oxidation or reduction of Bi(III) are very high being 39.8, 37.5 and 35.9 kcal/mol for the reactions 12, 13 and 14, respectively (Table 3), and, therefore, these routes may be ruled out.

$$[Bi^{III}(H_2O)_7(H_2O_2)](H_2O)^{3+} (\mathbf{3^{8}-H_2O}) \to [Bi^{IV}(H_2O)_7(OH)](H_2O)^{3+} + HO^{\bullet}$$
(12)

$$[\text{Bi}^{\text{III}}(\text{H}_2\text{O})_5(\text{OOH})](\text{H}_2\text{O})^{2^+} (\mathbf{4^6} \cdot \mathbf{H}_2\mathbf{O}) \to [\text{Bi}^{\text{III}}(\text{H}_2\text{O})_5](\text{H}_2\text{O})^{2^+} + \text{HOO}^{\bullet}$$
(13)

$$[\text{Bi}^{\text{III}}(\text{H}_2\text{O})_4(\text{H}_2\text{O}_2)(\text{OOH})](\text{H}_2\text{O})^{2+} (\mathbf{6}^6 - \mathbf{H}_2\mathbf{O}) \rightarrow [\text{Bi}^{\text{III}}(\text{H}_2\text{O})_4(\text{H}_2\text{O}_2)](\text{H}_2\text{O})^{2+} + \text{HOO}^{\bullet}$$
(14)

Additionally, the O–O bond cleavage in the OOH[–] ligand is also not favourable; the ΔG_s values of reactions 15 and 16 being 38.5 and 37.7 kcal/mol, respectively.

$$[Bi(H_2O)_5(OOH)](H_2O)^{2+} (4^6 - H_2O) \rightarrow [Bi(H_2O)_5(O)](H_2O)^{2+} + HO^{\bullet}$$
(15)

$$[Bi(H_2O)_4(H_2O_2)(OOH)](H_2O)^{2+} (\mathbf{6}^6 - \mathbf{H}_2 \mathbf{O}) \to [Bi(H_2O)_4(H_2O_2)(O)](H_2O)^{2+} + HO'$$
(16)

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(vi) Closure of the catalytic cycle. At the final steps of the catalytic cycle, the HOO' radical may be formed from complex 7^6 -H₂Ob to give [Bi(H₂O)₄(OH)](H₂O)²⁺ (8⁵-H₂O) (Scheme 8). The initial catalytic form is then restored as a result of the protonation of 8⁵-H₂O and subsequent water addition.

$$\begin{array}{c} HOO OH \\ [Bi(H_2O)_4]^{2+} \xrightarrow[-HOO]{} & OH \\ [Bi(H_2O)_4]^{2+} \xrightarrow[-HOO]{} & [Bi(H_2O)_4]^{2+} \xrightarrow[2H_2O]{} & H_2O \\ & I \\ [Bi(H_2O)_7]^{3+} \\ \hline & I^8 \end{array}$$

Scheme 8 Closure of the catalytic cycle.

(vii) Energy profile and activation energy. The energy profile for the whole process of the HO' radical formation is shown in Figure 11. Its inspection demonstrates that the rate limiting step of the HO' generation in the system $[Bi(H_2O)_8]^{3+}/H_2O_2$ is the monomolecular HO–OH bond cleavage in the key intermediate $[Bi(H_2O_4(H_2O_2)(OOH)](H_2O)^{2+}$ 6⁶-H₂O. The overall Gibbs free energy of activation relative to the initial level 1^8 -H₂O₂ is 15.2 kcal/mol. The estimate of the overall activation enthalpy ΔH_s^{\neq} is not that straightforward as the calculations of ΔG_s^{\neq} . Indeed, the energy of one of the reaction steps, *i.e.* hydrolysis, was calculated on the basis of the experimental pK_a value which is related to ΔG rather than to ΔH . However, assuming that the system entropy is not changed during the hydrolysis step, the overall activation enthalpy of the HO[•] formation should be 22.0 kcal/mol. This value correlates well with the experimentally determined effective activation energy of 20 ± 2.5 kcal/mol (see above).

(viii) Non-radical pathway. Additionally, the possibility of a non-radical mechanism involving the formation of Bi(V) species was also considered (the pathway similar to that proposed by Bray and Gorin for the Fenton system)⁴² (Scheme 9). However, all attempts to calculate the Bi(V) oxo-aqua-complexes $[Bi(H_2O)_n(=O)]^{3+}$ (n = 7, 5) failed. The geometry optimization always led to the hydroperoxo species indicating that the Bi(V) oxo-aqua-complexes are not stable and the coordinated water ligand should be spontaneously oxidized by Bi(V) to the peroxo derivatives. The equilibrium structure of the trihydroxo Bi(V) complex $[Bi(H_2O)_3(OH)_3](H_2O)^{2+}$ (9) was

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successfully found. However, the calculated ΔG_s value of its formation from $[Bi(H_2O)_7(H_2O_2)](H_2O)^{3+}$ is 24.1 kcal/mol what is clearly higher than the overall activation barrier of the free radical pathway discussed above (15.2 kcal/mol) (see ESI for details). Thus, the non-radical pathway based on the formation of Bi(V) species is not supported by theoretical calculations.



Scheme 9 Formation of Bi(V) complexes.

Final Remarks

In this work we demonstrated by both experimental and theoretical methods that the simple soluble Bi(III) salts – systems unexplored in the homogeneous oxidation of alkanes – exhibit a pronounced catalytic activity in this process. The yield of the oxygenates in the oxidation of cyclooctane catalysed by the system Bi(NO₃)₃/H₂O₂/HNO₃/CH₃CN+H₂O attains 32 % and the TON reaches 112. These results indicate that if even the simplest catalyst based on Bi is efficient in these processes, it is quite expected that the optimization of the catalysts and/or experimental conditions may significantly increase the efficiency of this system. Hence, further investigations of the Bi based catalysts in hydrocarbon chemistry are obviously important and welcome.

The obtained reaction selectivity parameters in the oxidation of certain linear and branched alkanes and the careful kinetic analysis indicated that the general mechanism of this reaction is the radical one with involvement of the highly reactive HO[•] radical which directly interacts with the alkane molecule (Scheme 2). The kinetic data and theoretical DFT calculations demonstrate that the

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generation of the HO' radicals in the catalytic system under study – the rate limiting step of the whole process – requires a relatively low activation energy (*ca.* 20 kcal/mol) and includes four principal steps, *i.e.* (*i*) substitution of a coordinated water molecule for H_2O_2 in the initial aqua complex, (*ii*) hydrolysis of the hydrogen peroxide adduct accompanied by the elimination of two coordinated water molecules, (*iii*) second H_2O -for- H_2O_2 substitution and (*iv*) homolytic HO–OH bond cleavage in the intermediate [Bi(H_2O)₄(H_2O_2)(OOH)]²⁺.

The relatively low activation energy of the HO[•] generation is accounted for by (*i*) the high lability of the Bi(III) aqua complexes (providing low activation energies of the water substitution steps), (*ii*) their high acidity (low ΔG_s value of the hydrolysis step) and (*iii*) the high activation of H₂O₂ in [Bi(H₂O)₄(H₂O₂)(OOH)]²⁺. The high activation of H₂O₂ in this intermediate is explained by the ability of the OOH⁻ ligand to be easily oxidized to HOO[•] and by delocalization of the spin electron density between two oxygen atoms of the OOH ligand in the product [M(H₂O)₄(OH)(OOH)[•]]²⁺ (Scheme 7). This mechanism does not require the change of the Bi oxidation state, while other pathways involving the change of the Bi oxidation state are significantly less favourable.

Comparison of the Bi catalyst with those based on other non-transition metals (Al, Ga, In, Be, Zn, Cd) investigated previously by experimental and/or theoretical methods^{2,3,19,20} indicate that the Bi(III) soluble salts are among the best catalytic systems in this series. Indeed, on one hand, the total yield of oxygenate products exceeds 30 % what is comparable with that obtained for the aluminum nitrate $(31 \ \%)^2$ and noticeably higher than for the Be, Zn and Cd systems (3–12 %).³ On the other hand, the theoretically calculated Gibbs free energy of activation is the lowest for the Bi catalyst.

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Graphical contents entry

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