



Hydroperoxidation of alkanes with hydrogen peroxide catalyzed by aluminium nitrate in acetonitrile [☆]

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ABSTRACT

The first example of alkane oxygenation with hydrogen peroxide catalyzed by a non-transition metal derivative (aluminium) is reported. Heating (70 °C) a solution of an alkane, RH, hydrogen peroxide (70% aqueous) and a catalytic amount of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in air for a few hours afforded the corresponding alkyl hydroperoxide, ROOH. With cyclooctane, the hydroperoxide yield attained 31% and the maximum turnover number was 150. It is proposed on the basis of measurements of the selectivity parameters for the oxidation of linear and branched alkanes and a kinetic study that the oxidation occurs with the participation of hydroxyl radicals.

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The oxidations of hydrocarbons with donors of an oxygen atom such as hydrogen peroxide, alkyl hydroperoxides and peroxy acids constitute an important field of contemporary catalytic chemistry, and some industrial processes are based on these reactions.¹ Derivatives of transition metals usually catalyze the oxygenations.² Only a few examples of catalysis by derivatives of non-transition metals have been reported. Thus, bismuth compounds, BiCl_3 and NaBiO_3 catalyze the oxidation of activated weak C–H bonds with TBHP.³ Solid aluminium oxide has been demonstrated to catalyze olefin epoxidation with hydrogen peroxide in ether or ethyl acetate.⁴ Wet alumina catalyzes the oxidation of phenyl sulfides to sulfoxides or sulfones,^{5a} and alicyclic ketones to lactones^{5b} and secondary alcohols to ketones^{5c} with Oxone. Diols are oxidized with sodium bromite in the presence of alumina.⁶ Soluble aluminium nitrate catalyzes olefin epoxidation with H_2O_2 in THF.⁷ Aluminium oxide^{8a} and aluminium trichloride^{8b} have been used to promote the Baeyer–Villiger oxidation of ketones with H_2O_2 . In the present work, we demonstrate for the first time that a soluble aluminium salt, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, is an efficient catalyst of alkane oxidation with hydrogen peroxide under relatively mild conditions.

$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (98% Aldrich) and 70% aqueous hydrogen peroxide ('Peróxidos do Brasil') were used as received. A stock solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 70% aqueous H_2O_2 (prepared at room temperature) was used in order to avoid introducing additional water into the reaction mixture. The oxidations of saturated hydrocarbons in acetonitrile were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was usually 5 mL. Typically, the reaction started when a portion of the catalyst stock solution in hydrogen peroxide was added in one portion to the solution of the substrate in MeCN. (*Caution*: the combination of air and H_2O_2 with organic compounds at elevated temperatures may be explosive!)

Samples of the reaction solutions were analyzed by GC. The oxygenation of alkanes gives rise to the formation of the corresponding alkyl hydroperoxides as the main products. To demonstrate the formation of alkyl hydroperoxides during this oxidation and to estimate their concentrations in the course of the reaction, we used a simple method developed earlier by some of us.⁹ If an excess of solid PPh_3 is added to a sample of the reaction solution, ca. 10 min before GC analysis, the alkyl hydroperoxide present is completely reduced to the corresponding alcohol. As a result, the chromatogram differs from that of a sample not subjected to the reduction (the alcohol peak rises, while the intensity of the ketone peak decreases). Comparing the intensities of peaks attributed to the alcohol and ketone before and after the reduction, it is possible to estimate the real concentrations of the alcohol, ketone and alkyl hydroperoxide present in the reaction solution.

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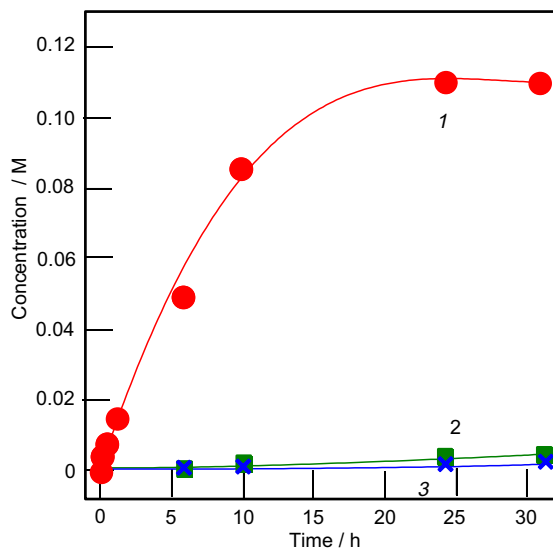


Figure 1. Accumulation of the products (cyclooctyl hydroperoxide, curve 1; cyclooctanol, curve 2; cyclooctanone, curve 3) in the oxidation of cyclooctane (0.5 M) with hydrogen peroxide (70% aqueous; 1.0 M; the total concentration of water in the reaction mixture was 1.3 M) catalyzed by $\text{Al}(\text{NO}_3)_3$ (1.0 mM) in MeCN at 70 °C. Concentrations of cyclooctanone and cyclooctanol were determined twice, before and after reduction of the aliquots with solid PPh_3 (for this method, see Ref. 9).

Our method has been employed by other chemists for the analysis of reaction products and detection of alkyl hydroperoxides during oxidations of C–H compounds by molecular oxygen, hydrogen peroxide and other peroxides.¹⁰ In the kinetic study of the cyclooctane oxidation, we measured the concentrations of cyclooctanone and cyclooctanol only after reduction with PPh_3 , because this reduction gives the most precise values of total concentrations of the products.

Heating a solution of cyclooctane in acetonitrile with 70% aqueous hydrogen peroxide in the presence of 1 mM $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

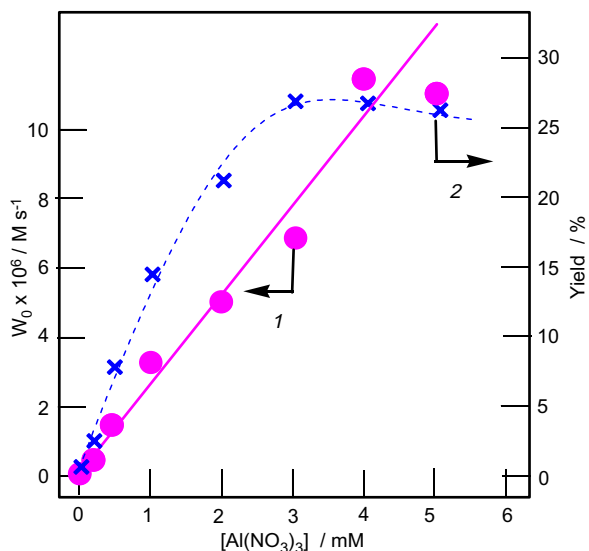


Figure 2. Oxidation of cyclooctane (0.5 M) with hydrogen peroxide (70% aqueous; 1.0 M; the content of water in the reaction mixture was 1.3 M) catalyzed by $\text{Al}(\text{NO}_3)_3$ in MeCN at 70 °C. Dependencies of the initial rate of oxygenate formation W_0 (curve 1) and total yield (%) of oxygenates (based on cyclooctane) after 10 h (curve 2) on the initial concentration of catalyst $\text{Al}(\text{NO}_3)_3$ are shown. Concentrations of cyclooctanone and cyclooctanol were determined after reduction of aliquots with solid PPh_3 . For the original full kinetic curves, see Figure S1.

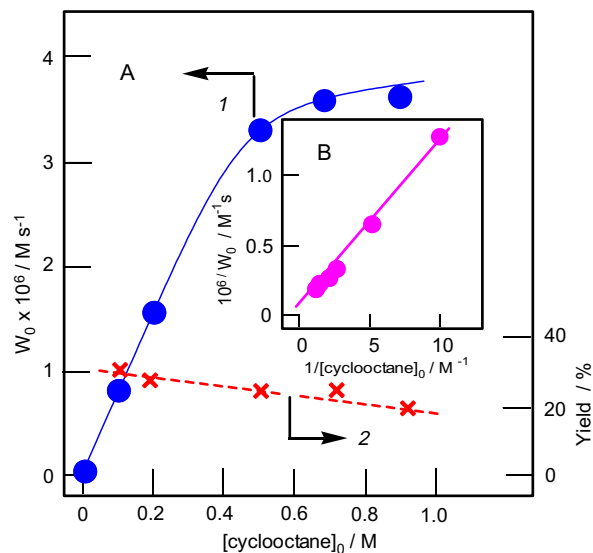


Figure 3. Oxidation of cyclooctane with hydrogen peroxide (70% aqueous; 1.0 M; the content of water in the reaction mixture was 1.3 M) catalyzed by $\text{Al}(\text{NO}_3)_3$ (1.0 mM) in MeCN at 70 °C. Graph A: Dependencies of the initial rate of oxygenate formation W_0 (curve 1) and total yield (%) of oxygenates (based on cyclooctane) after 32 h (curve 2) on initial concentration of cyclooctane are shown. Concentrations of cyclooctanone and cyclooctanol were determined after reduction of aliquots with solid PPh_3 . For the original full kinetic curves, see Figure S2. Graph B: Linear dependence of 1 using coordinates $1/W_0 - 1/[\text{cyclooctane}]_0$.

affords the cyclooctyl hydroperoxide, whereas cyclooctanone and cyclooctanol are formed in minor amounts (Fig. 1). Only negligible concentrations of the oxygenates were found in the absence of aluminium nitrate. The dependences of the oxygenation initial rate and the oxygenate yield on the initial concentration of the catalyst, cyclooctane and hydrogen peroxide are shown in Figures 2–4. The yield of cyclooctyl hydroperoxide attained 31% and the maximum

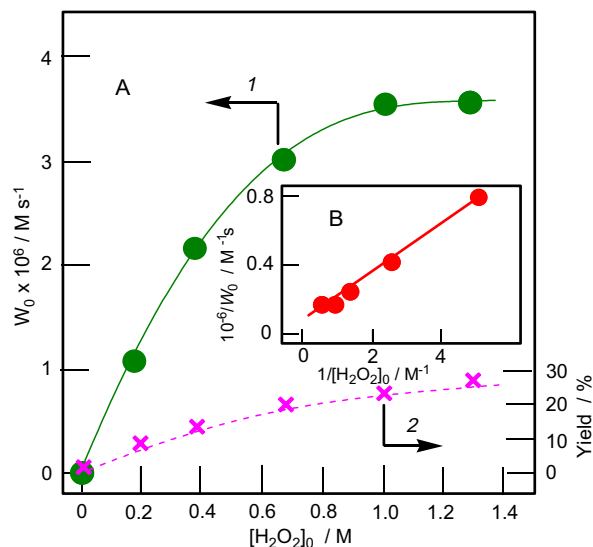


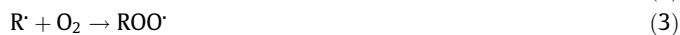
Figure 4. Oxidation of cyclooctane with hydrogen peroxide catalyzed by $\text{Al}(\text{NO}_3)_3$ (1.0 mM) in MeCN at 70 °C. Graph A: Dependencies of the initial rate of oxygenate formation W_0 (curve 1) and total yield (%) of oxygenates (based on cyclooctane) after 32 h (curve 2) on initial concentration of hydrogen peroxide are shown. The content of water in the reaction mixture was maintained constant (1.3 M) by adding water. Concentrations of cyclooctanone and cyclooctanol were determined after reduction of the aliquots with solid PPh_3 . For the original full kinetic curves, see Figure S3. Graph B: Linear dependence of 1 using coordinates $1/W_0 - 1/[\text{H}_2\text{O}_2]_0$.

turnover number was 150. It is interesting that in the initial period of the reaction, the catalyst exhibits some 'catalase' activity.

n-Octane can be hydroperoxidized by the system under discussion. The selectivity parameters for *n*-octane calculated from data in Table 1 and for *n*-heptane are low, C(1):C(2):C(3):C(4) \approx 1:5:5:5 (see Table 2). These values are close to the parameters determined previously for systems which oxidize alkanes with participation of hydroxyl radicals (compare with the parameters summarized in entries 2–6 of Table 2). It is clear that the corresponding selectivity parameters for the systems that do not involve active oxygen-centred radicals (entries 7–10) are noticeably higher. Bond-selectivity parameters in the Al-catalyzed reaction with branched alkanes (Table 3, entry 1), as in the case of linear alkanes, are close to the parameters found for the systems oxidizing alkanes with participation of hydroxyl radicals (compare with the parameters summarized in entries 2–6 of Table 3). The reaction proceeds non-stereoselectively: for the oxidation of both *cis*- and *trans*-1,2-dimethylcyclohexanes, the ratios of isomeric alcohols *trans/cis* (after reduction with PPh₃) were 0.8 (Table 3).

Thus, the data summarized in Tables 2 and 3 show that the selectivity parameters for oxidizing species generated by the H₂O₂–Al(NO₃)₃ system are close to the corresponding parameters found for the oxidation reaction with participation of hydroxyl radicals. It should be noted that the data shown in Figure 3 also support the assumption regarding the participation of hydroxyl radicals in alkane oxidation by the system under discussion. Indeed, the mode of dependence of the initial reaction rate on cyclooctane, RH, concentration indicates that RH and acetonitrile

compete for the oxidizing species, which is apparently a hydroxyl radical:



where W_i is the rate of the oxidizing species generation by the H₂O₂–Al(NO₃)₃ system, and steps (3) and (4) are not rate-limiting processes. Analysis of the above scheme in steady-state approximation relative to the hydroxyl radical led to the following equation for the RH oxidation rate:

$$-\frac{d[\text{RH}]}{dt} = \frac{d[\text{ROOH}]}{dt} = \frac{W_i}{1 + \frac{k_1[\text{MeCN}]}{k_2[\text{RH}]}} \quad (5)$$

Our experimental data are in good agreement with this equation: we found the linear dependence of $(d[\text{ROOH}]/dt)^{-1}$ and $[\text{cyclooctane}]_0^{-1}$, as shown in Figure 3, Graph B. It follows from this dependence that under the conditions described in the caption of Figure 3, the rate of active species generation W_i is equal to $7.5 \times 10^{-6} \text{ M s}^{-1}$ and the ratio $k_1[\text{MeCN}]/k_2 = 0.83 \text{ M}$. We should note that under the conditions of our experiments, competition between cyclooctane and hydrogen peroxide for the hydroxyl radical is not very probable because it is suspicious that the decrease of the rate constant for the interaction between HO \cdot and RH is more than 30-fold when the temperature is increased from 298 to

Table 1
Oxidation of *n*-octane^a

Time (h)	Products, concentration after reduction with PPh ₃ (mM)								TON	Yield (based on <i>n</i> -octane) (%)
	al-1	one-2	one-3	one-4	ol-1	ol-2	ol-3	ol-4		
2	0.02	0.49	0.52	0.30	1.9	3.7	3.8	3.4	14	3
10	0.11	0.49	0.58	0.50	3.8	14.2	14.1	12.8	47	9
24	0.19	1.17	1.43	1.24	4.7	18.3	17.7	15.8	61	12
32	0.23	1.52	1.95	1.60	6.8	19.9	19.1	16.9	68	14
38 ^b	0.00	0.00	0.00	0.00	0.00	0.0	0.0	0.0	–	0.3

^a Conditions: Al(NO₃)₃, 1 mM; *n*-octane, 0.5 M; H₂O₂, 1.0 M; 70 °C.

^b In the absence of Al(NO₃)₃.

Table 2
Selectivity parameters in the oxidation of linear alkanes by the 'H₂O₂/Al(NO₃)₃/MeCN' system as well as (for comparison) by certain other oxidizing systems^a

Entry	System	Parameter C(1):C(2):C(3):C(4)		
		<i>n</i> -Hexane	<i>n</i> -Heptane	<i>n</i> -Octane
1	H ₂ O ₂ –Al(NO ₃) ₃ (MeCN, 70 °C)		1:5.3:5.4:4.9	1:5.6:5.6:5.0
2	H ₂ O ₂ –hv (MeCN, 20 °C)	1:10:7	1:7:6:7	1:10.2:6.8:6.3
3	H ₂ O ₂ –FeSO ₄ (MeCN, 20 °C)		1:5:5:4.5	
4	H ₂ O ₂ – <i>n</i> -Bu ₄ NVO ₃ –PCA (MeCN, 40 °C) ^b	1:6.9:7.0	1:5.7:7.2:5.0	1:6.7:7.5:5.3
5	H ₂ O ₂ –Ni(ClO ₄) ₄ –TMTACN (MeCN, 70 °C) ^c		1:6.3:7.2:6.1	
6	H ₂ O ₂ – 1 (MeCN, 60 °C) ^d	1:6.2:7.1	1:5.5:5.0:4.6	
7	<i>m</i> -Chloroperoxybenzoic acid (MeCN, 25 °C)	1:36:36.5		
8	H ₂ O ₂ in CF ₃ COOH ^e	1:364:363		
9	H ₂ O ₂ –NaAuCl ₄ (MeCN, 75 °C) ^f		1:35:25:23	
10	H ₂ O ₂ – 2 –MeCO ₂ H (MeCN, 25 °C) ^g		1:46:35:34	1:29:25:24
11	TBHP– 2 –oxalic acid (MeCN, 50 °C) ^g		1:14:13:12	1:17:12:15

^a Parameters C(1):C(2):C(3):C(4) are relative normalized (i.e., calculated taking into account the number of hydrogen atoms at each carbon) reactivities of the hydrogen atoms at carbons 1, 2, 3 and 4, of the chain of linear alkanes. All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols.

^b For this system, which is believed to oxidize substrates via formation of hydroxyl radicals, see Ref. 12.

^c TMTACN is 1,4,7-trimethyl-1,4,7-triazacyclononane. For this system, see Ref. 13.

^d Compound **1** is the complex (2,3- η -1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium. For this system, see Ref. 14.

^e For this system, see Ref. 15.

^f For this system, see Ref. 16.

^g Compound **2** is the complex [Mn₂L₂(μ -O)₂]²⁺ where L is 1,4,7-trimethyl-1,4,7-triazacyclononane. For this system, see Ref. 17.

Table 3
Selectivity parameters in the oxidation of branched and cyclic alkanes by the 'H₂O₂/Al(NO₃)₃/MeCN' system as well as (for comparison) by certain other oxidizing systems^a

Entry	System	1°:2°:3° ^b				trans/cis ^c	
		2,2,4-TMP	MCH	2-MH	3-MH	cis-DMCH	trans-DMCH
1	H ₂ O ₂ -Al(NO ₃) ₃ (MeCN, 70 °C)	1:4.3:7.4	1:6:23			0.8	0.8
2	H ₂ O ₂ -hν (MeCN, 20 °C)	1:2:6	1:2:6	1:6:20	1:4:12	0.9	1.0
3	H ₂ O ₂ -FeSO ₄ (MeCN, 20 °C)	1:3:6				1.3	1.2
4	H ₂ O ₂ - <i>n</i> -Bu ₄ NVO ₃ -PCA (MeCN, 40 °C) ^b	1:1.5:10	1:9:37	1:14:64		0.75	0.8
5	H ₂ O ₂ -Ni(ClO ₄) ₄ -TMTACN (MeCN, 70 °C) ^c	1:2.3:4.5	1:7:15		1:5.3:55		
6	H ₂ O ₂ - 1 (MeCN, 60 °C) ^d	1:5:8.5	1:4:10	1:6:19		0.9	
7	<i>m</i> -Chloroperoxybenzoic acid (MeCN, 25 °C)	1:20:520	1:89:750			0.65	
8	H ₂ O ₂ in CF ₃ COOH ^e	1:52:0				RC	RC
9	H ₂ O ₂ -NaAuCl ₄ (MeCN, 75 °C) ^f	1:10:240	1:116:255	1:13:100			
10	H ₂ O ₂ - 2 -MeCO ₂ H (MeCN, 25 °C) ^g	1:5:55	1:26:200	1:19:204	1:22:200	0.34	4.1
11	TBHP- 2 -oxalic acid (MeCN, 50 °C) ^g	1:0.4:32	1:0.3:0.6			0.2	7.3

^a Parameters 1°:2°:3° are relative normalized reactivities of the hydrogen atoms at primary, secondary and tertiary carbons of branched alkanes. Abbreviations: 2,2,4-TMP, 2,2,4-trimethylpentane (isooctane); MCH, methylcyclohexane; 2- and 3-MH, 2- and 3-methylhexanes. Parameter *trans/cis* is the ratio of *trans*- and *cis*-isomers of *tert*-alcohols formed in the oxidation of dimethylcyclohexanes (*cis*-DMCH and *trans*-DMCH). All parameters were measured after reduction of the reaction mixtures with triphenylphosphine before GC analysis and calculated based on the ratios of isomeric alcohols.

^b For this system, which is believed to oxidize substrates via formation of hydroxyl radicals, see Ref. 12.

^c TMTACN is 1,4,7-trimethyl-1,4,7-triazacyclonane. For this system, see Ref. 13.

^d Compound **1** is the complex (2,3-η-1,4-diphenylbut-2-en-1,4-dione)undecacarbonyl triangulotriosmium. For this system, see Ref. 14.

^e For this system, see Ref. 15. RC, retention of configuration.

^f For this system, see Ref. 16.

^g Compound **2** is the complex [Mn₂L₂(μ-O)₂]²⁺ where L is 1,4,7-trimethyl-1,4,7-triazacyclonane. For this system, see Ref. 17.

343 K. This could be probable but only if the activation energy is equal to 64 kJ/mol which is not typical for reactions with participation of hydroxyl radicals. The ratio $k_1/k_2 = 4.5 \times 10^{-2}$ obtained in our experiments is in satisfactory agreement with calculated constants at 298 K previously measured in independent experiments. Thus in accord with Ref. 11 the $k_1(\text{MeCN} + \text{HO}^\bullet)/k_2(\text{cyclooctane} + \text{HO}^\bullet)$ ratio is equal to 1.3×10^{-2} , and we can conclude that our kinetic data also support the assumption about the participation of hydroxyl radicals in the reaction under discussion.

Additional information on the reaction mechanism can be obtained from analysis of the dependence of the initial oxidation rate on the initial hydrogen peroxide concentration. This dependence, as illustrated in Figure 4, is in good agreement with the assumption that a peroxo complex¹⁸ of Al³⁺ with H₂O₂ (conventionally denoted below as 'Al³⁺·H₂O₂') takes part in the active species generation step. Indeed, assuming that in a polar medium the salt Al(NO₃)₃ is present in completely dissociative form, and based on Eq. 6



we can propose the following mechanism for the active species generation:



Using this proposal in the quasi-equilibrium approximation for the peroxo complex, we can deduce the following equation for the rate W_{ROOH} of ROOH formation at [cyclooctane]₀ = 0.7 M:

$$W_{\text{ROOH}} = 2k_{i\text{-eff}} \frac{k_7[\text{H}_2\text{O}_2]_0[\text{Al}^{3+}]_0}{1 + k_7[\text{H}_2\text{O}_2]_0} \quad (9)$$

We introduce here the effective constant value $k_{i\text{-eff}}$ which is different from the true value k_i because under the conditions of our experiments at [cyclooctane]₀ = 0.7 M, the hydrocarbon does not accept all the hydroxyl radicals generated in reaction (8).

The experimental data shown in Figure 4 are in good agreement with Eq. 9: we found a linear dependence of $(W_{\text{ROOH}})^{-1}$ on $[\text{H}_2\text{O}_2]^{-1}$ (see Fig. 4, Graph B). This dependence allowed us to determine $k_{i\text{-eff}} = 3.8 \times 10^{-3} \text{ s}^{-1}$ from the segment which is cut on the y-axis. The equilibrium constant for peroxo complex formation $K_7 = 1.4 \text{ M}^{-1}$ was also measured from the tangent of this straight line slope taking into account the value of the segment mentioned above.

The efficient rate constant for hydroxyl radical generation was determined at [cyclooctane]₀ = 0.7 M, where in accord with data shown in Figure 3, ca. 50% of all the generated hydroxyl radicals are accepted by the substrates present in the reaction solution. As a consequence, we can calculate the true value of the constant $k_i = 2k_{i\text{-eff}} = 7.6 \times 10^{-3} \text{ s}^{-1}$.

The details of scheme presented by Eqs. 7, 8, 2–4 at the moment are unclear. We cannot also exclude the transient formation of aluminium derivatives in 'exotic' valent state. For example, the couple Al(III)/Al(II) could be responsible for hydroxyl radical generation. Previously, we proposed a similar mechanism with the V(V)/V(VI) manifold which generates hydroperoxyl and hydroxyl radicals from hydrogen peroxide.¹²

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Supplementary data

Supplementary data (Figs. S1–S3) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.058.

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