

# Alkane oxygenation with hydrogen peroxide catalysed by soluble derivatives of nickel and platinum<sup>†</sup>

Georgiy B. Shul'pin\*

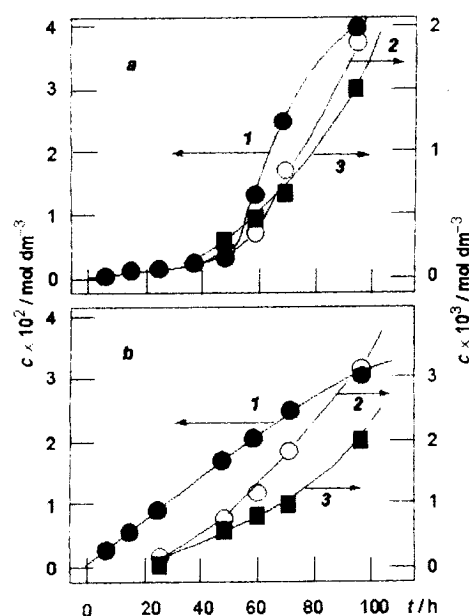
Semenov Institute of Chemical Physics, Russian Academy of Sciences, ul. Kosygina, dom 4,  
Moscow 119991, Russia

Various alkanes can be oxidised by hydrogen peroxide in acetonitrile solution at 70°C if Ni(ClO<sub>4</sub>)<sub>2</sub> (in the presence of 1,4,7-trimethyl-1,4,7-triazacyclononane) or H<sub>2</sub>PtCl<sub>6</sub> are used as catalysts; whereas the nickel-catalysed reaction seems to proceed *via* attack of hydroxyl radicals on an alkane, the oxidation in the presence of platinum occurs possibly with participation of oxo or peroxy derivatives of this metal.

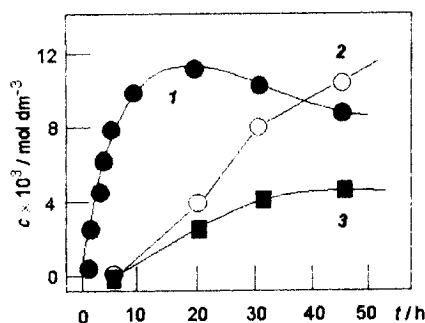
**Keywords:** alkanes, catalysis, hydrogen peroxide, nickel, platinum

Derivatives of various transition metals are known to catalyse alkane oxidations by hydrogen peroxide.<sup>1</sup> Complexes of iron and manganese are the most carefully studied catalysts.<sup>1</sup> Recently we have described alkane oxidations by systems based on derivatives of manganese,<sup>2</sup> vanadium,<sup>3</sup> osmium,<sup>4</sup> chromium<sup>5</sup> and gold.<sup>6</sup> Although nickel complexes were used as catalysts in oxidations of olefins,<sup>7</sup> ketones,<sup>8</sup> ethers,<sup>9</sup> dye amarant<sup>10</sup> and ethylbenzene<sup>11</sup> only a few examples of alkane oxidations catalysed by nickel-containing systems<sup>12</sup> as well as aliphatic hydroxylation by a bis(μ-oxo)dinickel(III) complex<sup>13</sup> have been published. Epoxidation of alkenes was promoted by various nickel(II) complexes of macrocyclic ligands (*e.g.*, cyclam).<sup>14</sup> On the other hand, the nickel-containing tetrapyrrole, factor F430, isolated from *Methanobacterium thermoautotrophicum* is the prosthetic group of methyl coenzyme M reductase.<sup>15</sup> This enzyme catalyses the transformation of the thioether methyl coenzyme M to give methane. The reversed reaction could be the methane activation process. Thus it was very interesting to explore a possibility of nickel complexes to catalyse alkane oxidations.

In the present study we used nickel(II) perchlorate as a catalyst and hydrogen peroxide (in the form of 35% aqueous solution) as an oxidant. All reactions<sup>16</sup> were carried out in acetonitrile solution at 70°C. The samples of reaction solutions were analysed twice (before and after their treatment with PPh<sub>3</sub>) by GC which showed<sup>1–6,17</sup> that alkyl hydroperoxides were main products whereas concentrations of the corresponding alcohols and ketones were much lower. The hydroperoxidation of cyclooctane proceeds very slowly with significant auto-acceleration after 50 hours (Fig. 1a). However a small amount of 1,4,7-trimethyl-1,4,7-triazacyclononane, TMTACN (which could be considered as a model of some nitrogen-containing macrocycles found in nature, *e.g.*, tetrapyrrole) dramatically enhances the reaction rate in the beginning of the oxidation (Fig. 1b). It should be noted that bis(1,4,7-triazacyclononane)nickel(III) oxidizes hydrogen peroxide.<sup>18</sup> Unfortunately, after 50–70 hours TMTACN is substantially decomposed and the rate of oxidation gradually descends. Nevertheless, the turnover number attains 66 after 96 hours: The oxidation of *n*-heptane under the same conditions after 28 hours and after reduction with PPh<sub>3</sub> gave (mol/dm<sup>3</sup>) heptanol-1 (0.00017), heptanol-2 (0.0007), heptanol-3 (0.0008), heptanol-4 (0.00034) as well as some heptanoic acid. It is interesting that addition of picolinic acid



**Fig. 1** Accumulation of cyclooctyl hydroperoxide (curves 1), cyclooctanone (2) and cyclooctanol (3) in the oxidations of cyclooctane (0.15 mol/dm<sup>3</sup>) with H<sub>2</sub>O<sub>2</sub> (0.45 mol/dm<sup>3</sup>) in acetonitrile at 70°C catalysed by Ni(ClO<sub>4</sub>)<sub>2</sub> (5 × 10<sup>-4</sup> mol/dm<sup>3</sup>) in the absence (graph a) and in the presence of TMTACN (0.0012 mol/dm<sup>3</sup>) (b).



**Fig. 2** Accumulation of cyclooctyl hydroperoxide (1), cyclooctanone (2) and cyclooctanol (3) in the oxidations of cyclooctane (0.15 mol/dm<sup>3</sup>) with H<sub>2</sub>O<sub>2</sub> (0.45 mol/dm<sup>3</sup>) in acetonitrile at 70°C catalysed by H<sub>2</sub>PtCl<sub>6</sub> (5 × 10<sup>-4</sup> mol/dm<sup>3</sup>).

\* To receive any correspondence. E-mail: Shulpin@chph.ras.ru

<sup>†</sup> This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

**Table 1** Oxidation of certain hydrocarbons with hydrogen peroxide in acetonitrile at 70°C catalysed by Ni(ClO<sub>4</sub>)<sub>4</sub> – 1,4,7-trimethyl-1,4,7-triazacyclononane, H<sub>2</sub>PtCl<sub>6</sub> and some other systems<sup>a</sup>

Hydrocarbon/ selectivity parameter <sup>b</sup>	Systems for hydrocarbon oxidation				
	Ni(ClO <sub>4</sub> ) <sub>4</sub> – TMTACN	H <sub>2</sub> PtCl <sub>6</sub>	VO <sub>3</sub> <sup>-</sup> – PCA <sup>c</sup>	[LMn <sup>IV</sup> (O <sub>3</sub> )Mn <sup>IV</sup> L] <sup>2+</sup> – CH <sub>3</sub> COOH <sup>d</sup>	Fe(ClO <sub>4</sub> ) <sub>3</sub> <sup>e</sup>
<i>n</i> -Heptane/ C(1):C(2):C(3):C(4)	1:6.3:7.2:6.1		1:6.2:6.3:5.3	1:45.6:35.3:34.7	
3-Methylhexane/ 1°:2°:3°	1:5.3:55	1:7.0:180	1:5.7:24.7	1:22:220	1:4.3:30
Methylcyclohexane/ 1°:2°:3°	1:7.0:15	1:7.4:28	1:6.0:18	1:26:200	1:7.5:43
2,4,4-Trimethylpentane/ 1°:2°:3°	1:2.3:4.5	1:8.0:50	1:4.0:8.0	1:4.5:60	1:5.2:45
<i>cis</i> -Decalin/ <i>trans/cis</i>	4.7		4.3	0.12	
Toluene/ <i>o:m:p</i>	32:45:23		50:23:27	38:18:44	60:26:14

<sup>a</sup>The concentrations of reaction products were measured after reduction with PPh<sub>3</sub>. <sup>b</sup>Parameter C(1):C(2):C(3):C(4) is normalised (*i.e.*, calculated taking into account the number of hydrogen atoms at each position) relative reactivities of hydrogen atoms at positions 1, 2, 3 and 4 of the hydrocarbon chain, respectively. Parameter 1°:2°:3° is normalised relative reactivities of hydrogen atoms at primary, secondary and tertiary carbons, respectively. Parameter *trans/cis*=[*trans*-decal-9-ol]/[*cis*-decal-9-ol], *i.e.*, the ratio of concentrations of *trans*-decal-9-ol and *cis*-decal-9-ol formed in the oxidation of *cis*-decalin. Parameter *o:m:p* is the non-normalised ratio of concentrations of *ortho*-, *meta*-, and *para*-cresols formed in the reaction. <sup>c</sup>PCA, pyrazine-2-carboxylic acid. The oxidation at 30°C. For this system, see refs 1, 3. <sup>d</sup>L = TMTACN. The oxidation at 20°C. For this system, see refs 1 and 2. <sup>e</sup>At room temperature.

(5 × 10<sup>-4</sup> mol/dm<sup>3</sup>) instead of TMTACN almost completely depressed the cyclooctane oxidation (only 0.004 mol/dm<sup>3</sup> of cyclohexyl hydroperoxide obtained after 96 hours).

In order to get a mechanistic understanding of this process, we studied the oxidation of some assay alkanes. The results are summarized in Table 1. To compare these data, the corresponding parameters for some other systems are also given. Thus, it is believed that the oxidations by the system H<sub>2</sub>O<sub>2</sub> – VO<sub>3</sub><sup>-</sup> – pyrazine-2-carboxylic acid proceed *via* the formation of hydroxyl radicals which attack C–H bonds of the alkane. On the contrary, alkane oxygenations by the H<sub>2</sub>O<sub>2</sub> – [(TMTACN)Mn<sup>IV</sup>(O<sub>3</sub>)Mn<sup>IV</sup>(TMTACN)]<sup>2+</sup> – CH<sub>3</sub>COOH system apparently involve the interaction of the C–H bonds with Mn<sup>V</sup>=O species. It follows from Table 1 that oxidations by the system H<sub>2</sub>O<sub>2</sub> – Ni(ClO<sub>4</sub>)<sub>2</sub> – TMTACN exhibit very low selectivities for *n*-heptane and branched alkanes and the reaction with *cis*-decalin is not stereoselective. These data testify clearly that Ni(II)-catalysed alkane oxygenation proceeds mainly with participation of free hydroxyl radicals.

We have also investigated alkane oxidations with H<sub>2</sub>O<sub>2</sub> catalysed by H<sub>2</sub>PtCl<sub>6</sub>. An example of arene hydroxylation with H<sub>2</sub>O<sub>2</sub> catalysed by cationic complexes of platinum(II) has been reported in the literature.<sup>19</sup> The kinetics of Pt(IV)-catalysed oxidation are shown in Fig. 2. It can be seen that, in comparison with the analogous Ni(II)-catalysed process, this reaction proceeds much more rapidly and concentrations of relatively stable cyclooctanol and cyclooctanone are high. The turnover number attains 44 after 44 hours.

It is noteworthy that the reaction catalysed by Pt(IV) exhibits noticeably higher selectivities for branched alkanes (see Table 1) than that determined for the H<sub>2</sub>O<sub>2</sub> – Ni(ClO<sub>4</sub>)<sub>2</sub> – TMTACN and H<sub>2</sub>O<sub>2</sub> – VO<sub>3</sub><sup>-</sup> – PCA systems. The parameters for Pt(IV) are lower than that determined for the H<sub>2</sub>O<sub>2</sub> – [(TMTACN)Mn<sup>IV</sup>(O<sub>3</sub>)Mn<sup>IV</sup>(TMTACN)]<sup>2+</sup> – CH<sub>3</sub>COOH system and close to values obtained for Fe(III)-catalysed oxidations. For the latter case one could assume the participation in the oxidation of both hydroxyl radicals and Fe<sup>V</sup>=O species. Analogously, on the basis of the selectivity parameters we can conclude that the alkane oxidation catalysed by Pt(IV) at least in one of possible routes involves not free hydroxyl radicals but oxo or peroxo complexes of platinum.

The author thanks the Russian Basic Research Foundation (Project No. 98-03-32015a) for support.

Received 12 October 2001; accepted 5 February 2002  
Paper 01/1085

## References

- A.E. Shilov and G.B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer, Dordrecht/Boston/London, 2000; A.E. Shilov and G.B. Shul'pin, *Chem. Rev.*, 1997, **97**, 2879.
- (a) J.R. Lindsay Smith and G.B. Shul'pin, *Tetrahedron Lett.*, 1998, **39**, 4909; (b) G.B. Shul'pin and J.R. Lindsay Smith, *Russ. Chem. Bull.*, 1998, **47**, 2379; (c) G.B. Shul'pin, G. Süß-Fink and J.R. Lindsay Smith, *Tetrahedron*, 1999, **55**, 5345; (d) G.B. Shul'pin, G. Süß-Fink and L.S. Shul'pina, *J. Mol. Catal. A: Chem.*, 2001, **170**, 17. (e) G.B. Shul'pin, *Neftekhimiya*, 2001, **41**, 440.
- G.B. Shul'pin, D. Attanasio and L. Suber, *Russ. Chem. Bull.*, 1993, **42**, 55; G.B. Shul'pin, A.N. Druzhinina and G.V. Nizova, *Russ. Chem. Bull.*, 1993, **42**, 1327; G.V. Nizova and G.B. Shul'pin, *Russ. Chem. Bull.*, 1994, **43**, 1146; G.B. Shul'pin and G. Süß-Fink, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1459; G.B. Shul'pin, R.S. Drago and M. Gonzalez, *Russ. Chem. Bull.*, 1996, **45**, 2386; M.C. Guerreiro, U. Schuchardt and G.B. Shul'pin, *Russ. Chem. Bull.*, 1997, **46**, 749; G.B. Shul'pin, M.C. Guerreiro and U. Schuchardt, *Tetrahedron*, 1996, **52**, 13051; G.V. Nizova, G. Süß-Fink and G.B. Shul'pin, *Tetrahedron*, 1997, **53**, 3603; U. Schuchardt, M.C. Guerreiro and G.B. Shul'pin, *Russ. Chem. Bull.*, 1998, **47**, 247; G. Süß-Fink, G.V. Nizova, S. Stanislas and G.B. Shul'pin, *J. Mol. Catal. A: Chem.*, 1998, **130**, 163; G.B. Shul'pin, Y. Ishii, S. Sakaguchi and T. Iwahama, *Russ. Chem. Bull.*, 1999, **48**, 887; G.B. Shul'pin, Yu.N. Kozlov, G.V. Nizova, G. Süß-Fink, S. Stanislas, A. Kitaygorodskiy and V.S. Kulikova, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1351; Yu.N. Kozlov, G.V. Nizova and G.B. Shul'pin, *Russ. J. Phys. Chem.*, 2001, **75**, 770.
- G.B. Shul'pin, G. Süß-Fink and L.S. Shul'pina, *Chem. Commun.*, 2000, 1131.
- G.B. Shul'pin, G. Süß-Fink and L.S. Shul'pina, *J. Chem. Res. (S)*, 2000, 576.
- G.B. Shul'pin, A.E. Shilov and G. Süß-Fink, *Tetrahedron Lett.*, 2001, **42**, 7253.
- H. Yoon and C.J. Burrows, *J. Am. Chem. Soc.*, 1988, **110**, 4087; T. Yamada, T. Takai, O. Rhode and T. Mukaiyama, *Chemistry Lett.*, 1991, 1; R. Irie, Y. Ito and T. Katsuki, *Tetrahedron Lett.*, 1991, **32**, 6891.

- 8 T. Yamada, K. Takahashi, K. Kato, T. Takai, S. Inoki and T. Mukaiyama, *Chemistry Lett.*, 1991, 641.
- 9 A.M. Romano and M. Ricci, *J. Mol. Catal., A: Chem.*, 1997, **120**, 71.
- 10 P.M. Paradis, *J. Chem. Res. (S)*, 1999, 340.
- 11 L.I. Matienko and I.A. Mosolova, *Russ. Chem. Bull.*, 1999, **48**, 55.
- 12 T. Iwahama, K. Syojyo, S. Sakaguchi and Y. Ishii, *Org. Proc. Res. & Dev.*, 1998, **2**, 255.
- 13 S. Itoh, H. Bandoh, S. Nagamoto, T. Kitagawa and S. Fukuzumi, *J. Am. Chem. Soc.*, 1999, **121**, 8945.
- 14 D. Lee, H. Bang and M.P. Suh, *J. Mol. Catal., A: Chem.*, 2000, **151**, 71.
- 15 M. Zimmer and R.H. Crabtree, *J. Am. Chem. Soc.*, 1990, **112**, 1062; L. Signor, C. Knappe, R. Hug, B. Schweizer, A. Pfaltz and B. Jaun, *Chem. Eur. J.*, 2000, **6**, 3508; T. Wondimagegn and A. Ghosh, *J. Am. Chem. Soc.*, 2000, **122**, 6375; C.J. Campbell, J.F. Rusling and C. Brückner, *J. Am. Chem. Soc.*, 2000, **122**, 6679; T. Wondimagegn and A. Ghosh, *J. Am. Chem. Soc.*, 2001, **123**, 1543.
- 16 In order to determine concentrations of all alkane oxidation products the samples of reaction solutions were analysed twice (before and after their treatment with PPh<sub>3</sub>) by GC (LKhM-80-6, columns 2 m with 5% Carbowax 1500 on 0.25–0.315 mm Inerton AW-HMDS; carrier gas argon) measuring concentrations of the corresponding alcohol and ketone. This method described by us earlier<sup>1–6,17</sup> allows to detect alkyl hydroperoxides and to measure also the real concentrations of all three products (alkyl hydroperoxide, alcohol and aldehyde or ketone) present in the reaction solution, because usually alkyl hydroperoxides are decomposed in the gas chromatograph to produce mainly the corresponding alcohol and ketone.
- 17 G.B. Shul'pin and A.N. Druzhinina, *React. Kinet. Catal. Lett.*, 1992, **47**, 207; G.B. Shul'pin and G.V. Nizova, *React. Kinet. Catal. Lett.*, 1992, **48**, 333; G.B. Shul'pin and A.N. Druzhinina, *Petrol. Chem.* 1993, **33**, 247; G.B. Shul'pin, A.N. Druzhinina and L.S. Shul'pina, *Petrol. Chem.*, 1993, **33**, 321; G.B. Shul'pin, D. Attanasio and L. Suber, *J. Catal.*, 1993, **142**, 147; G.B. Shul'pin, M.M. Bochkova and G.V. Nizova, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1465; G.B. Shul'pin, G.V. Nizova and Yu.N. Kozlov, *New J. Chem.*, 1996, **20**, 1243.
- 18 N. Koshino, S. Funahashi and H.D. Takagi, *J. Chem. Soc., Dalton Trans.*, 1997, 4175.
- 19 A. Marsella, S. Agapakis, F. Pinna and G. Strukul, *Organometallics*, 1992, **11**, 3578.