Organic Chemistry

Oxidation with the "O_2—H_2O_2—VO_3^-—pyrazine-2-carboxylic acid" reagent

6.* Oxidation of n-heptane and cyclohexane. Direct determination of alkyl hydroperoxides by gas-liquid chromatography

M. C. Guerreiro,[a] U. Schuchardt,[a] and G. B. Shul'pin[b]*

[a]*Instituto de Quimica, Universidade Estadual de Campinas, Caixa Postal 6154,*
13083-970 Campinas (São Paulo), Brazil.
Fax: + (55) 192 393 805
[b]*N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: 007 (095) 938 2156

n-Heptane is readily oxidized in acetonitrile under the action of H_2O_2 with a "vanadate anion—pyrazine-2-carboxylic acid" system as the catalyst in air to form isomeric heptyl hydroperoxides (detected by GLC) along with isomeric heptanols and heptanones. Heptyl hydroperoxides slowly decompose at low temperature yielding the corresponding alcohols and ketones (aldehyde). The values of the parameter of the relative normalized reactivity of the H atoms at the carbon atoms in positions 1, 2, 3, and 4 depend on the reaction time and concentrations of the reagents. The value of the parameter of selectivity $C(1) : C(2) : C(3) : C(4)$ varies in the range from $1.0 : 2.8 : 2.9 : 1.8$ to $1.0 : 5.6 : 5.9 : 5.3$. The low selectivity of the reaction shows that the key role is played by the attack of highly reactive radical particles on the C—H bond of the alkane molecule.

Key words: metallocomplex catalysis, oxidation, hydrogen peroxide, vanadium complexes, alkanes, n-heptane, cyclohexane, activation of C—H bonds.

Tetra-n-butylammonium vanadate efficiently catalyzes the aerobic oxidation of alkanes and other organic compounds (for instance, arenes and alcohols) by hydrogen peroxide in acetonitrile in the presence of pyrazine-2-carboxylic acid (PCA).[1-7] At low (room)

temperatures, the corresponding alkyl hydroperoxide is mainly formed. This peroxide then slowly decomposes into a ketone and an alcohol. In the oxidation of cyclohexane, the quantity of cyclohexyl hydroperoxide, cyclohexanol, and cyclohexanone present in the reaction mixture were estimated only from chromatographic analysis by comparing data obtained prior to and after

* For Part 5, see Ref. 1.

reduction with triphenylphosphine.[1—10] It should be noted that no direct determination of alkyl hydroperoxides by GLC was performed in our previous studies. It was also shown that atmospheric oxygen participates in this reaction, and when it is absent, no oxygenation occurs. The oxidation of cyclohexane in an atmosphere of $^{18}O_2$ provided convincing evidence that the oxidation products contain a considerable amount of ^{18}O.[11,12] Thus, one can conclude that hydrogen peroxide is a promoter in the oxidation of alkanes, and atmospheric oxygen plays the role of oxidant.

In the present work, we report the results of studies of changes in the selectivity of the oxidation of *n*-heptane as a function of reaction time, temperature, and concentrations of reagents as well as the direct quantitative determination of the principal primary oxidation products (all isomeric heptyl hydroperoxides) by GLC. The oxidation of cyclohexane was also studied.

Experimental

The oxidation of *n*-heptane was carried out in air in cylindrical 30-mL glass vessels with vigorous stirring at constant temperature. Normally, 30% aqueous hydrogen peroxide (Peróxido do Brasil S/A, São Paulo) (0.2 mL, 0.2 mol L^{-1})

was added to a solution of the catalyst (in all cases 0.1 mmol L^{-1} $Bu^n_4NVO_3$ and 0.4 mmol L^{-1} PCA) and a hydrocarbon in MeCN.

The reaction mixture was analyzed by GLC before and after addition of an excess of solid triphenylphosphine. The analysis was carried out using a Hewlett—Packard Series II, 5890 chromatograph equipped with a quartz-reinforced injector, a flame ionization detector, a quartz Carbowax 20M column (25 m × 0.2 mm; 0.2 μm), and a Shimadzu CR3A integrator. Helium was used as the carrier gas. Preliminary calibrations were performed using solutions of the oxidation products of known concentrations. The peaks on the chromatograms were identified by chromato-mass-spectrometry using a Shimadzu GC-17A-QP 5000 GLC-MS instrument (INNOWAX, 25 m×0.2 mm; 0.4 μm); the mass spectra were compared with those of authentic samples (Wiley 139 Database Library).

Acetonitrile of HPLC grade (99.99%, EM Science, Darmstadt), and *n*-heptane and cyclohexane (99.9%, Aldrich) were used without additional purification.

Results and Discussion

The oxidation of *n*-heptane was carried out at 7, 23, 61, and 80 °C at optimal concentrations of the vanadate (0.1 mmol L^{-1}) and PCA (0.4 mmol L^{-1}) determined previously.[1—7,11,12] The results obtained are listed in Table 1.

Table 1. Oxidation of *n*-heptane with the "O_2—H_2O_2—VO_3^-—PCA" reagent in MeCN[a]

T/°C	Time /h	Concentration of the products[b]/mmol L^{-1}								Content[c] of 2b (%)	Selectivity[d] C(2) : C(3) : C(4)
		Alcohols				Carbonyl compounds					
		3a	**3b**	**3c**	**3d**	**4a**	**4b**	**4c**	**4d**		
7	68	0.9	3.6	3.7	1.6	0.14	0.07	0.12	0.05	96	5.3 : 5.5 : 4.8
	119	2.3	9.9	10.0	4.55	0.45	0.2	0.3	0.15	95	5.5 : 5.6 : 5.1
	140	2.4	10.6	11.0	4.95	0.5	0.25	0.35	0.15	95	5.6 : 5.9 : 5.3
23	1	0.34	1.19	1.12	0.51	0.11	0.03	0.05	0.02	95	4.1 : 3.9 : 3.5
	2	0.51	1.91	1.88	0.85	0.20	0.06	0.09	0.04	94	4.2 : 4.2 : 3.8
	3	0.78	3.01	2.98	1.36	0.34	0.10	0.15	0.06	93	4.2 : 4.2 : 3.8
	4	1.0	4.0	4.0	1.8	0.5	0.15	0.2	0.1	93	4.2 : 4.2 : 3.8
	7	1.4	5.55	5.55	2.5	0.6	0.2	0.3	0.15	93	4.3 : 4.4 : 4.0
	9	1.7	7.2	7.3	3.3	0.8	0.3	0.4	0.2	92	4.5 : 4.6 : 4.2
	22	2.75	11.3	11.5	5.2	1.25	0.45	0.65	0.3	92	4.4 : 4.6 : 4.1
	51	3.65	15.3	15.7	7.0	1.4	0.6	0.8	0.4	92	4.8 : 5.0 : 4.5
61	0.17	2.3	10.0	8.9	4.0	1.6	1.1	1.7	0.7	78	4.3 : 4.1 : 3.6
	0.5	2.9	14.2	12.6	5.7	2.8	2.5	3.6	1.5	65	4.4 : 4.3 : 3.8
	0.67	3.2	14.9	13.0	5.9	2.9	2.9	4.1	1.7	60	4.4 : 4.2 : 3.7
	1.0	3.1	14.7	12.5	6.4	2.9	3.0	4.4	1.8	55	4.4 : 4.2 : 4.1
80	0.05	1.2	6.2	6.0	2.6	1.65	0.9	1.2	0.45	71	3.7 : 3.8 : 3.2
	0.1	1.2	5.85	5.5	2.4	1.9	1.25	1.75	0.7	57	3.4 : 3.5 : 3.0
	0.15	1.2	6.0	5.7	2.5	1.9	1.55	2.1	0.8	50	3.6 : 3.8 : 3.2
	0.25	1.15	5.85	5.5	2.45	1.95	1.65	2.3	0.9	45	3.6 : 3.8 : 3.2
	0.5	1.1	5.15	4.75	2.1	1.65	1.65	2.15	0.9	35	3.7 : 3.8 : 3.3
	0.75	1.1	4.7	4.25	1.95	1.45	1.65	2.1	0.85	30	3.7 : 3.7 : 3.3
	1.5	1.2	4.7	4.4	2.0	1.65	2.0	2.5	1.0	20	3.5 : 3.6 : 3.2

[a] Concentrations: *n*-heptane, 0.46 mol L^{-1}; H_2O_2, 0.2 mol L^{-1}; $Bu^n_4NVO_3$, 0.1 mmol L^{-1}; PCA, 0.4 mmol L^{-1}. [b] The concentrations of the isomers were determined by GLC after treatment with triphenylphosphine. [c] The relative content of heptan-2-yl hydroperoxide (**2b**) in the mixture of products of oxidation at position 2 was estimated both from a comparison of the concentrations of alcohols and ketones before and after addition of PPh_3 and from the intensities of the peaks of the corresponding hydroperoxides on the chromatograms. [d] Relative normalized reactivities of the H atoms at C(2), C(3), and C(4) atoms (the reactivity of the H atom at the C(1) atom was assumed to be equal to 1.0) with allowance for the number of H atoms at each of the C atoms.
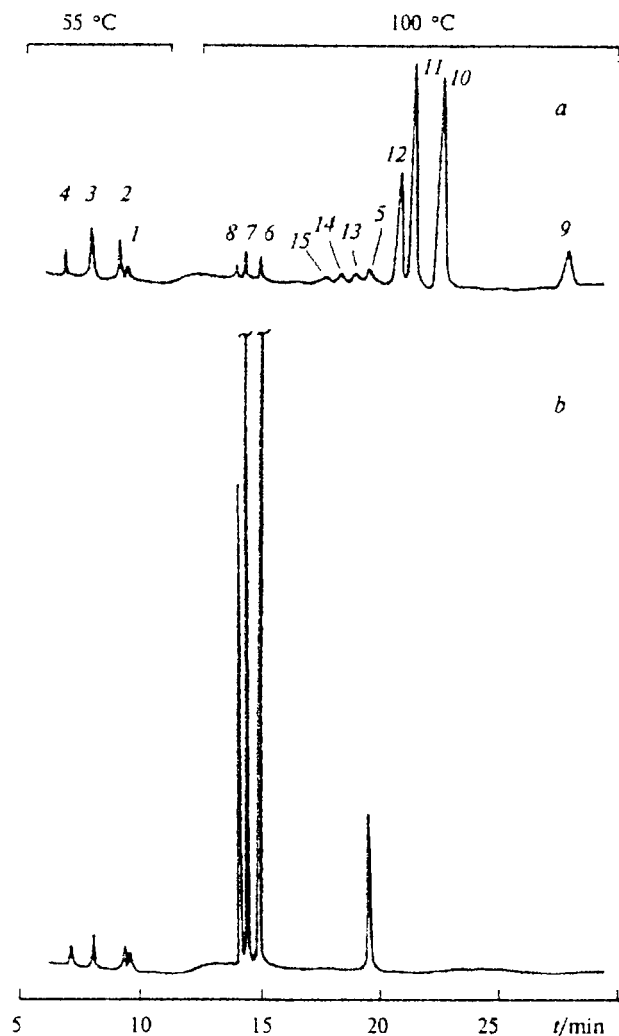
Fig. 1. GLC of the products of the oxidation of heptane (0.46 mol L^{-1}) with the "O$_2$—H$_2$O$_2$—VO$_3$$^-$—PCA" reagent in MeCN (23 °C, 3 h) before (*a*) and after (*b*) their reduction with triphenylphosphine. Peaks: *1* — heptanal; *2—4* — heptanone (2-, 3-, and 4-isomers, respectively); *5—8* — heptanol (1-, 2-, 3-, and 4-isomers, respectively); *9—12* — heptyl hydroperoxide (1-, 2-, 3-, and 4-isomers, respectively); *13—15* — unidentified peroxide products.

In contrast to previous works, in the present work we analyzed the composition of the alkyl hydroperoxides formed in the oxidation by GLC. Direct determination of unstable alkyl hydroperoxides becomes possible when quartz-reinforced injectors are used for the chromatograph and quartz columns (see, for instance, Refs. 7,8). The use of metal (steel or copper) injector and columns most often results in full decomposition of alkyl hydroperoxides with the formation of the corresponding ketones and alcohols (often in a ratio close to 1 : 1). Four peaks corresponding to isomeric heptyl hydroperoxides

were observed on the chromatograms of the reaction mixture along with less intense peaks of isomeric alcohols and ketones (aldehyde) (Fig. 1). The order of retention times of isomeric hydroperoxides is the same sequence as that of the corresponding alcohols and ketones (the retention time increases on going from 4- to 3-, 2-, and 1-isomers). After reduction of the sample with excess solid triphenylphosphine, the peaks of heptyl hydroperoxides completely disappear, and a great increase in the intensity of all the peaks corresponding to the isomeric alcohols is simultaneously observed (see Fig. 1). The intensity of all the peaks due to ketones decreases, which is evidence for a slight (10—15%) decomposition of heptyl hydroperoxides in the chromatograph. Peaks *13*, *14*, and *15* (see Fig. 1) probably belong to isomeric peroxides, heptane derivatives, since they completely disappear after reduction with PPh$_3$.

In the oxidation of cyclohexane we also observed a peak of cyclohexyl hydroperoxide for the first time. A comparison of the chromatograms of the samples ob-
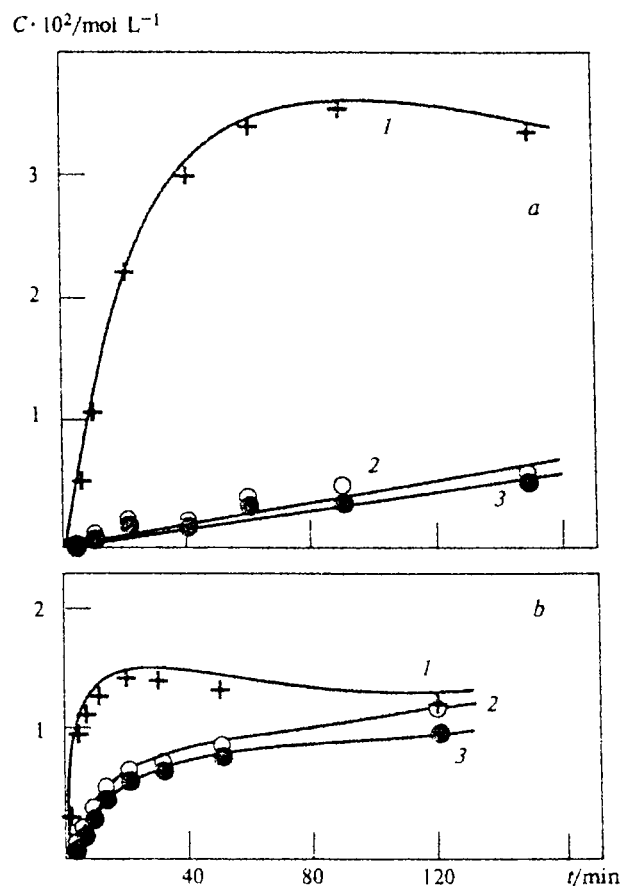

Fig. 2. Kinetic curves of the accumulation of cyclohexyl hydroperoxide (*1*) and of its decomposition with the formation of cyclohexanol (*2*) and cyclohexanone (*3*) in the oxidation of cyclohexane (0.46 molL^{-1}) with the "O$_2$—H$_2$O$_2$—VO$_3$$^-$—PCA" reagent in MeCN at 50 (*a*) and 70 °C (*b*).

tained before and after reduction with PPh_3 allowed us to calibrate the chromatograms and to determine directly the concentrations of all three oxidation products, *viz.*, alkyl hydroperoxide, ketone, and alcohol. As follows from Fig. 2, stable products, cyclohexanone and cyclohexanol, are formed simultaneously with cyclohexyl hydroperoxide in the oxidation of cyclohexane. When the oxidation with participation of H_2O_2 is over (about 3 h at 50 or 70 °C), decomposition of cyclohexyl hydroperoxide begins, yielding numerous unidentified products.

In the present work the oxidation of *n*-heptane (1) was studied in more detail. The above noted relative instability of isomeric heptyl hydroperoxides 2 (they undergo some decomposition, approximately 10—15%, resulting in alcohols 3 and carbonyl compounds 4, even in the case of quartz columns) and the formation of small amounts of unidentified peroxide products preclude precise determination of the concentrations of peroxides. Thus, to achieve higher accuracy in measuring the selectivity of oxidation, we determined the concentrations of isomers after their reduction by PPh_3 (Scheme 1). The parameters obtained are given in Table 1. Nevertheless, it should be emphasized that the content of isomeric 2 in the reaction mixture can be estimated by both direct determination of the intensities of their peaks on the chromatograms and by measurements of the intensities of the peaks of the corresponding carbonyl compounds and alcohols before and after reduction by triphenylphosphine.

Scheme 1

$$CH_3(CH_2)_5CH_3$$

1
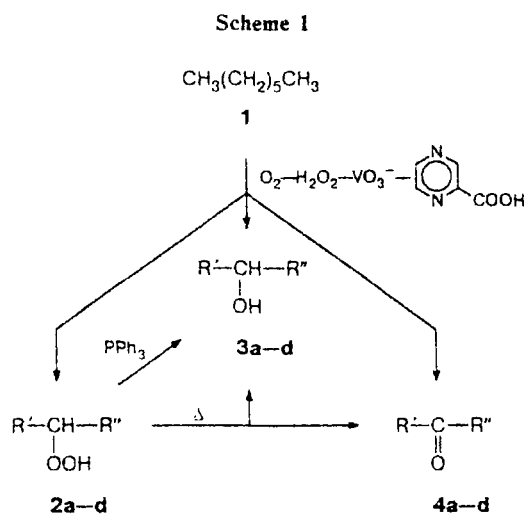
a: $R' = CH_3(CH_2)_5$, $R'' = H$
b: $R' = CH_3(CH_2)_4$, $R'' = CH_3$
c: $R' = CH_3(CH_2)_3$, $R'' = CH_2CH_3$
d: $R' = CH_3(CH_2)_2$, $R'' = (CH_2)_2CH_3$

As follows from Table 1, the rate of oxidation sharply increases as the temperature increases. The observed activation energy estimated from these data is

92 ± 10 kJ mol^{-1}. Only very slow decomposition of 2 occurs at 23 °C. The rate of decomposition of hydroperoxide at elevated temperatures (61 and 80 °C) is comparable with the rate of its formation. The optimal temperature for attaining the maximum yield of the oxidation products is 23 °C. The total yield of oxidation products after 51 h is 22.4% with respect to H_2O_2 (moles per mole of H_2O_2) and 10% with respect to 1. The total turnover number of the catalyst is 450. The overall concentration of all the oxidation products at high temperatures (61 and 80 °C) is appreciably lower. This might be due to unproductive decomposition of H_2O_2 into water and molecular oxygen catalyzed by vanadium.

Oxidation of 1 proceeds with low selectivity, the relative reactivity of the C—H bonds at the C(1), C(2), C(3), and C(4) atoms is ~1 : 4 : 4 : 4. This value is close to that found for the oxidation of 1 by H_2O_2 in MeCN (23 °C, 1 h) under the action of UV-irradiation (1.0 : 3.4 : 3.2 : 3.0). The low selectivity for vanadate-catalyzed oxidation by hydrogen peroxide confirms the assumption that the hydroxyl radicals play a key role in this oxygenation of alkanes. Actually, it is likely that the HO˙ radical abstracts the H atom from the alkane RH, which results in the alkyl radical R˙. The latter rapidly reacts with an O_2 molecule to give the peroxyl radical ROO˙, which is subsequently converted into an alkyl hydroperoxide, a ketone, or an alcohol. The relative content of the two last products increases at elevated temperatures.

Thus, the "O_2—H_2O_2—VO_3^-—pyrazine-2-carboxylic acid" reagent in MeCN is likely to be a very efficient "generator of hydroxyl radicals" (see, for instance, Ref. 13). However, the mechanism of the generation of hydroxyl radicals, as well as that of the transformation of peroxyl radicals into alkyl hydroperoxide, is not clear. It should be noted that the oxidation of alkanes by H_2O_2 catalyzed by iron complexes[14] is much more selective in the case of *n*-hexane: C(1) : C(2) : C(3) = 1 : >35 : >40; the value of this parameter for analogous phenylselenation of *n*-hexane is 1.0 : 5.4 : 5.6.[15]

As follows from Table 1, the parameter of selectivity C(1) : C(2) : C(3) : C(4) does not remain constant and changes in the course of the reaction from the minimum value (1.0 : 3.5 : 3.6 : 3.2) 1.5 h after the beginning of the reaction at 80 °C to the maximum value (1.0 : 5.6 : 5.9 : 5.3) after 140 h at 7 °C. In general, it can be noticed that the C(*N*) : C(1) (*N* = 2, 3, 4) ratios gradually and monotonically increase in the course of the reaction and have appreciably higher values when the reaction is carried out at low temperatures. This may be associated with the partial oxidation of 4a to the corresponding acid, which results in a decrease in the concentration of 1-isomers in the reaction mixture. However, the C(*N*) : C(1) ratios remain constant (or even slightly decrease) in the course of the reaction at 80 °C, during the period when no accumulation of oxidation products occurs. It is of interest that the C(2) to C(3) ratio is less than 1 in almost all cases (except for

Table 2. Dependence of the yield of oxygenation products on the initial concentration of *n*-heptane in its oxidation with the "O_2—H_2O_2—VO_3^-—PCA" reagent in MeCN[a]

[Heptane]$_0$ /mol L^{-1}	Concentration of the products[b]/mmol L^{-1}								Overall concentration of all products /mmol L^{-1}	Content[c] of 2b (%)	Selectivity[d] C(2) : C(3) : C(4)
	Alcohols				Carbonyl compounds						
	3a	3b	3c	3d	4a	4b	4c	4d			
					[H$_2$O$_2$]$_0$ = 0.05 mol L^{-1}						
0.12	0.16	0.75	0.68	0.15	0.35	0.21	0.29	0.16	2.75	44	2.8 : 2.9 : 1.8
0.23	0.46	2.05	1.94	0.89	0.53	0.26	0.38	0.17	6.68	70	3.5 : 3.5 : 3.2
0.46	0.41	1.93	1.76	0.80	0.77	0.22	0.35	0.16	6.40	77	2.7 : 2.7 : 2.4
0.55	0.59	2.51	2.36	1.07	0.62	0.20	0.31	0.14	7.80	84	3.4 : 3.3 : 3.0
					[H$_2$O$_2$]$_0$ = 0.20 mol L^{-1}						
0.06	0.32	1.43	1.33	0.63	0.54	0.34	0.56	0.21	5.36	52	3.1 : 3.1 : 2.9
0.12	0.59	2.38	2.27	1.04	0.59	0.30	0.43	0.19	7.79	75	3.4 : 3.4 : 3.1
0.23	0.76	2.94	2.96	1.33	0.46	0.18	0.27	0.12	9.78	88	3.8 : 4.0 : 3.6
0.46	1.02	3.81	3.70	1.67	0.39	0.11	0.17	0.08	10.95	94	4.1 : 4.1 : 3.7
0.55	0.99	3.77	3.89	1.71	0.43	0.10	0.18	0.08	11.15	95	4.1 : 4.3 : 3.8

[a] Conditions: 23 °C; 3 h. Concentrations of the components: Bu$^n_4$NVO$_3$, 0.1 mmol L^{-1}; PCA, 0.4 mmol L^{-1}. [b] The concentrations of the isomers were determined by GLC after the addition of triphenylphosphine to a sample of the reaction solution. [c] The relative content of heptan-2-yl hydroperoxide; see footnote[c] to Table 1. [d] Relative normalized reactivities of H atoms; see footnote[d] to Table 1.

the reaction at 61 °C). The methylene group in position 2 of the *n*-heptane chain is bonded to the less electron-donating methyl group, and the CH$_2$ group in position 3 is bonded to the electron-rich ethyl group. Therefore, it can be assumed that at low temperatures the electron effect of the substituent dominates over steric hindrances when the C—H bond is attacked by hydroxyl radicals (*i.e.*, the rate of hydroxylation of position 3 is higher). The C(3) : C(4) ratio varies only a little in the course of the reaction.

The data in Table 2 show the dependence of the initial oxidation rate (defined as the concentration of oxidation products in the initial period of the reaction) on the initial concentration of **1**. When the concentrations of both reactants are comparable ([H$_2$O$_2$] =

0.20 mol L^{-1}), a monotonic decrease in the initial rate with the increase in [1]$_0$ is observed. If **1** is in excess ([H$_2$O$_2$] = 0.05 mol L^{-1}), the reaction rate is proportional to the concentration of the substrate at a low concentration of heptane; at [1]$_0$ > 0.2 mol L^{-1}, this rate is almost independent of the concentration of the hydrocarbon.

At a relatively high concentration of H$_2$O$_2$ (0.20 mol L^{-1}), the C(N) : C(1) ratios depend on the initial concentration of **1** and increase from ~3 : 1 to ~4 : 1 if [1]$_0$ varies from 0.06 to 0.55 mol L^{-1}. It is important to note that the relative content of isomers **2** in the mixture of the products increases from 52 to 95% in parallel with the change in selectivity. This can be explained by the existence of competing reactions be-

Table 3. Dependence of the yield of oxygenation products on initial concentration of H$_2$O$_2$ in the oxidation of *n*-heptane with the "O_2—H_2O_2—VO_3^-—PCA" reagent in MeCN[a]

[H$_2$O$_2$]$_0$ /mol L^{-1}	Concentration of products[b]/mmol L^{-1}								Overall concentration of all products /mmol L^{-1}	Content[c] of 2b (%)	Selectivity[d] C(2) : C(3) : C(4)
	Alcohols				Carbonyl compounds						
	3a	3b	3c	3d	4a	4b	4c	4d			
0.01	0.12	0.48	0.39	0.18	0.23	0.08	0.13	0.05	1.66	67	2.4 : 2.2 : 2.0
0.05	0.33	1.26	0.96	0.45	0.30	0.09	0.14	0.06	3.59	85	3.2 : 2.6 : 2.4
0.10	0.72	3.08	2.92	1.32	0.86	0.24	0.38	0.17	9.69	85	3.2 : 3.1 : 2.8
0.15	1.06	3.35	3.04	1.60	0.60	0.20	0.32	0.10	10.27	88	3.2 : 3.1 : 3.0
0.20	1.04	3.86	3.71	1.71	0.35	0.12	0.19	0.08	11.06	94	4.3 : 4.2 : 3.9
0.40	0.72	2.53	2.66	1.21	0.22	0.12	0.13	0.06	7.65	91	4.2 : 4.4 : 4.0
0.50	0.58	1.30	1.28	0.60	0.05	0.25	0.28	0.12	3.88	70	3.7 : 3.7 : 3.4
0.50[e]	0.05	0.13	0.15	0.09	0.21	0.73	0.74	0.37	2.47	64	5.0 : 5.2 : 5.2

[a] Conditions: 23 °C; 3 h. Concentrations of the components: *n*-heptane, 0.46 mol L^{-1}; Bu$_4$NVO$_3$, 0.1 mmol L^{-1}; PCA, 0.4 mmol L^{-1}. [b] The concentrations of the isomers were determined by GLC after the addition of triphenylphosphine to a sample of the reaction solution. [c] The relative content of heptan-2-yl hydroperoxide; see footnote[c] to Table 1. [d] Relative normalized reactivities of H atoms; see footnote[d] to Table 1. [e] The concentration of *n*-heptane is 0.06 mol L^{-1}.

tween the catalyst and either RH or ROOH. In fact, if a vanadium-containing catalyst participates in the formation and decomposition of the alkyl hydroperoxide, the rate of its decomposition is lower at high concentrations of RH.

The dependence of the initial rate of oxidation on the initial concentration of H_2O_2 is bell-shaped with a maximum at $[H_2O_2]_0 = 0.20$ mol L^{-1} (Table 3). At low concentrations of H_2O_2 (<0.1 mol L^{-1}), the reaction rate is approximately proportional to the concentration of the oxidant. The reason for the decrease in the yield of oxidation products at high concentration of H_2O_2 is obscure and calls for further investigations.

We determined the balance of the reaction masses at a comparatively low concentration of the hydrocarbon. At $[1]_0 = 54.6$ mmol L^{-1} and $[H_2O_2]_0 = 0.20$ mol L^{-1}, the mass balance is 99.4% after 3 h at 23 °C.

Compared to other systems based on H_2O_2 or/and O_2 and using complexes of transition metals as catalysts,[14-32] the "$O_2-H_2O_2-VO_3^-$—pyrazine-2-carboxylic acid" reagent exhibits noticeably higher efficiency and oxidizes the methyl group of the alkane at a relatively high rate (compared with the methylene group).

References

1. G. B. Shul'pin, R. S. Drago, and M. Gonzalez, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2514 [*Russ. Chem. Bull.*, 1996, 45, 2386 (Engl. Transl.)].
2. G. B. Shul'pin, D. Attanasio, and L. Suber, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 64 [*Russ. Chem. Bull.*, 1993, 42, 55 (Engl. Transl.)].
3. G. B. Shul'pin, D. Attanasio, and L. Suber, *J. Catal.*, 1993, 142, 147.
4. G. B. Shul'pin, A. N. Druzhinina, and G. V. Nizova, *Izv. Akad. Nauk, Ser. Khim.*, 1993, 1394 [*Russ. Chem. Bull.*, 1993, 42, 1326 (Engl. Transl.)].
5. G. V. Nizova and G. B. Shul'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1212 [*Russ. Chem. Bull.*, 1994, 43, 1146 (Engl. Transl.)].
6. G. B. Shul'pin and G. Süss-Fink, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1459.
7. G. B. Shul'pin, M. C. Guerreiro, and U. Schuchardt, *Tetrahedron*, 1996, 52, 13051.
8. N. M. Emanuel' and D. Gal, *Okislenie etilbenzola* [*Oxidation of Ethylbenzene*], Nauka, Moscow, 1984, 280 pp. (in Russian).
9. G. B. Shul'pin, M. M. Bochkova, and G. V. Nizova, *J. Chem. Soc., Perkin Trans. 2*, 1995, 1465.
10. G. B. Shul'pin, G. V. Nizova, and Yu. N. Kozlov, *New J. Chem.*, 1996, 20, 1243.
11. G. V. Nizova, G. Süss-Fink, and G. B. Shul'pin, *J. Chem. Soc., Chem. Commun.*, 1997, 397.
12. G. V. Nizova, G. Süss-Fink, and G. B. Shul'pin, *Tetrahedron*, 1997, 53, 3603.
13. B. A. Aveline, I. E. Kochevar, and R. W. Redmond, *J. Am. Chem. Soc.*, 1996, 118, 289.
14. C. Sheu, S. A. Richert, P. Cofré, B. Ross, Jr., A. Sobkowiak, D. T. Sawyer, and J. R. Kanofsky, *J. Am. Chem. Soc.*, 1990, 112, 1936.
15. C. Sheu, A. Sobkowiak, L. Zhang, N. Ozbalik, D. H. R. Barton, and D. T. Sawyer, *J. Am. Chem. Soc.*, 1989, 111, 8030.
16. P. E. Ellis, Jr. and J. E. Lyons, *Coord. Chem. Rev.*, 1990, 105, 181.
17. U. Schuchardt, C. E. Z. Krähembühl, and W. A. Carvalho, *New J. Chem.*, 1991, 15, 955.
18. A. S. Goldstein and R. S. Drago, *J. Chem. Soc., Chem. Commun.*, 1991, 21.
19. L.-C. Kao, A. C. Hutson, and A. Sen, *J. Am. Chem. Soc.*, 1991, 113, 700.
20. M. Lin and A. Sen, *J. Am. Chem. Soc.*, 1992, 114, 7307.
21. A. Sen and M. Lin, *J. Chem. Soc., Chem. Commun.*, 1992, 508.
22. A. Sen, M. Lin, L.-C. Kao, and A. C. Hutson, *J. Am. Chem. Soc.*, 1992, 114, 6385.
23. U. Schuchardt, W. A. Carvalho, and E. V. Spinacé, *Synlett*, 1993, 713.
24. J. A. Labinger, *Catal. Lett.*, 1994, 26, 95.
25. M. W. Grinstaff, M. G. Hill, J. A. Labinger, and H. B. Gray, *Science*, 1994, 264, 1311.
26. K. Nakata, Y. Yamaoka, T. Miyata, Y. Taniguchi, K. Takaki, and Y. Fujiwara, *J. Organomet. Chem.*, 1994, 473, 329.
27. A. S. Goldstein, R. H. Beer, and R. S. Drago, *J. Am. Chem. Soc.*, 1994, 116, 2424.
28. M. Lin and A. Sen, *Nature*, 1994, 368, 613.
29. M. Kurioka, K. Nakata, T. Jintoku, Y. Taniguchi, K. Takaki, and Y. Fujiwara, *Chem. Lett.*, 1995, 244.
30. D. H. R. Barton and D. K. Taylor, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 595 [*Russ. Chem. Bull.*, 1995, 44, 575 (Engl. Transl.)].
31. E. R. Birnbaum, M. W. Grinstaff, J. A. Labinger, J. E. Bercaw, and H. B. Gray, *J. Mol. Catal., A: Chem.*, 1995, 104, L119.
32. A. E. Shilov and G. B. Shul'pin, *Aktivatsiya i kataliticheskie reaktsii uglevodorodov* [*Activation and Catalytic Reactions of Hydrocarbons*], Nauka, Moscow, 1995, 400 pp. (in Russian).