INTERACTION OF HYDROPEROXIDES WITH Cu(II) IONS IN AQUEOUS MEDIUM

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Hydroperoxides (HPs) react with Cu(I) ions, generating alkoxyl radicals

$$\mathrm{ROOH} + \mathrm{Cu(I)} \rightarrow \mathrm{RO}^{\cdot} + \mathrm{Cu(II)} + \mathrm{HO}^{-} \qquad (1)$$

Cu(II) ions, because of the low oxidation–reduction potential (ORP) of the pair Cu^{2+}/Cu^{+}, cannot generate peroxyl radicals from HPs [1] through the reaction

$$\mathrm{ROOH} + \mathrm{Cu(II)} \rightarrow \mathrm{ROO}^{\cdot} + \mathrm{Cu(I)} + \mathrm{H}^{+} \qquad (2)$$

Known examples of HP decomposition in the presence of Cu(II) salts have been explained by their thermolysis, accompanied by the formation of alkyl radicals and reduction of Cu(II) to Cu(I) by these radicals [2]. Along with this, the decomposition of HPs can also take place under the influence of Cu(II) salts under conditions such that there can be no thermal decomposition [3].

Here we are reporting on a study of the reactions of H_2O_2, n-propyl hydroperoxide, tetrahydro-2-furyl hydroperoxide, and 2-methyltetrahydro-2-furyl hydroperoxide (I) with Cu(II) salts in aqueous medium at 20°C, with the aim of determining the factors responsible for the decomposition of HPs under the influence of Cu(II) ions, the development of a low-temperature method for the generation of functionally substituted alkyl radicals, and investigation of their oxidative conversions.

It was established that the HP decomposition rate is very much dependent on the nature of the ligands bonded to the Cu(II), the structure of the HP, and the pH of the medium. In aqueous solutions of $Cu(NO_3)_2$, $Cu(ClO_4)_2$, or $Cu(BF_4)_2$, the HPs decompose slowly at 20°C. This may be related to initiation of the reaction by Fe(III) present as a trace impurity, the content of which is 0.005 mole % as determined by atomic absorption. One fact that supports this view is that the initiation rate ($W_i = 4.7 \cdot 10^{-10}$ mole/liter·sec) calculated in accordance with [4] for H_2O_2 (0.1 mole/liter) and Fe(III) ($1 \cdot 10^{-6}$ mole/liter) at pH 3.0, I = 0.06 mole/liter, 25°C, is in satisfactory agreement with the value that we obtained ($W_i = 5 \cdot 10^{-10}$ mole/liter·sec).

Thus, aquo ions of Cu(II), which do not form stable complexes with NO_3^-, ClO_4^-, or BF_4^-, obviously cannot bring about the decomposition of HPs. In contrast, complexes with the anions Cl^-, Br^-, CN^-, SCN^-, N_3^-, or NO_2^- bring about rapid decomposition of HPs at 20°C. The decomposition will take place in a relatively stable system such as $Cu(NO_3)_2-HP-H_2O$ if a salt containing a complexing anion is added. When the Cu(II) ions are complexed, the solution color changes. The possibility of occurrence of reaction (2) in the presence of halides and pseudo-halides is related to the fact that complex formation caused by the indicated ligands gives better stabilization of the reduced form Cu(I). This leads to an increase in the ORP of the electron pair $Cu^+ = Cu^{2+} + e$, −0.153 V; $CuCl = Cu^{2+} + Cl^- + e$, −0.538 V; $CuBr = Cu^{2+} + Br^- + e$, −0.640 V; $CuCN = Cu^{2+} + CN^- + e$, −1.12 V) [5].

However, the ORPs that are developed in this case are insufficient to generate peroxyl radicals from the HP in the undissociated form ($H_2O_2 = HO_2^{\cdot} + H^+ + e$, −1.43 V) [5]. Therefore, we can assume that the HPs in this system react in a dissociated form, since the ROO^- anion is a better electron donor than the undissociated HP ($HO_2^- = HO_2^{\cdot} + e$, −0.74 V) [6].

Protolytic dissociation of the HP (I) in the presence of Cu(II) aquo ions is supported by the results from potentiometric measurements. It can be seen from Fig. 1 that the Cu(II) ion and HP concentrations are linearly related to the amount of H^+ released. An increase in the level of acidic properties of the HP in the presence of Cu(II) has a direct effect on their complex formation

$$\mathrm{ROOH} + (\mathrm{Cu(H_2O)_6})^{2+} \rightleftarrows (\mathrm{ROOCu(H_2O)_5})^{+} + \mathrm{H_3O}^{+} \qquad (3)$$

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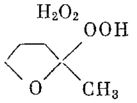
TABLE 1. Dependence of Initial Initiation Rate on Nature of HP and Halide [ROOH 100, Cu(II) 20, TNM 2, C_2H_5OH = 300 mmoles/liter; 25°C]

Hydroperoxide	pK_a	pH	Added salt, mmoles/liter	$W_i \cdot 10^9$, moles/liter·sec
t-BuOOH	12,8	3,00	NaCl, 100	13,4
H_2O_2	11,6	3,00	The same	26,1
	11,4±0,1	3,00	"	28,2
The same	11,4±0,1	3,50	NaF, 40	2,5
"	11,4±0,1	3,50	NaCl, 40	27,7
"	11,4±0,1	3,50	NaBr, 40	79

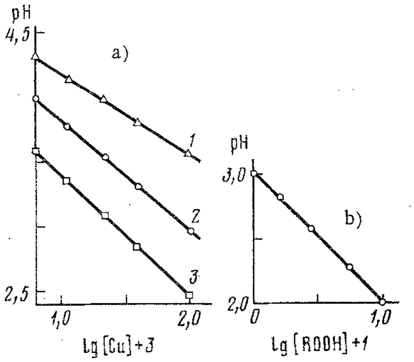


Fig. 1

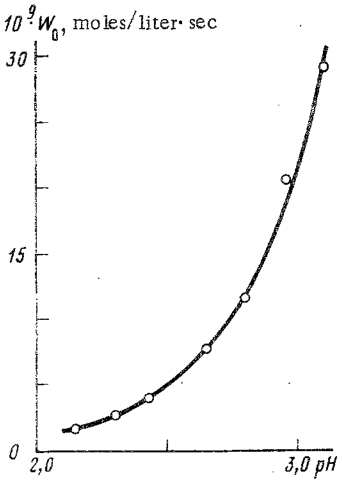


Fig. 2

Fig. 1. Interaction of Cu(II) aquo ions with 2-methyltetrahydro-2-furyl hydroperoxide (20°C, I = 3.0 moles/liter $LiNO_3$). Graph a: influence of Cu(II) concentration on pH change, with following HP concentrations, moles/liter: 1) 0; 2) 0.200; 3) 0.333. Graph b: influence of HP concentration on pH change, [Cu(II)] = 0.10 mole/liter.

Fig. 2. Initial rate of decomposition of 2-methyltetrahydro-2-furyl hydroperoxide as a function of pH ([HP] = 100, $[Cu^{2+}]$ = 20, $[Cl^-]$ = 100, $[C_2H_5OH]$ = 300, and [TNM] = 2 mmoles/liter; 25°C).

The slopes of the lines in Fig. 1 on these particular coordinates are 1.0 ± 0.2, indicating the formation of a complex of the HP (I) with Cu(II) with a 1/1 composition. From these data, when we take into account the coordination number of the central ion, we can represent the composition of the mixed complex of Cu(II) with the anion of the hydroperoxide and inorganic ligands by the formula $(ROOCu(II)X_n(H_2O)_{5-n})^{(1-n)+}$ (n = 1-3). The process rate is determined by the concentration of the complex-bonded HP, which in turn depends on the nature of the HP and the pH of the medium. With increasing acid properties of the HP, with other conditions equal, the equilibrium of reaction (3) is shifted to the right. As can be seen from Table 1, the lower the value of pK_a, the higher is the initial rate of initiation of HP decomposition in the systems that were studied, measured in the presence of tetranitromethane (TNM). In acidic solutions (pH < 2), owing to the shift of the equilibrium (3) to the left, the reaction is almost completely stopped (Fig. 2). In the 2.0-2.5 pH interval, the initial initiation rate is proportional to $1/[H^+]$. At pH 2.5-3.5, owing to partial hydrolysis of the Cu(II) complex, the initiation rate is proportional to $1/[H^+]^n$, where n = 1-1.3.

At pH > 3.5, owing to hydrolysis of the Cu(II) complex, the homogeneity of the system breaks down.

The decomposition of the HP (I) under the influence of Cu(II) chloro complexes leads mainly to 3-chloropropyl acetate (II) and 3-acetopropanol (III). The increasing yield of the chloride (II) with increasing Cl^- concentration (Fig. 3) can be explained by an increase in the relative amount of catalytically active Cu(II) chloro complexes. After essentially all of the Cu(II) ions had been bound into the complex, further increases in the Cl^- content do not affect the yield of the chloride (II).

TABLE 2. Products from Decomposition of 2-Methyltetrahydro-2-furyl Hydroperoxide under the Influence of Cu(II) Complexes

Anion X	Products, moles/mole hydroperoxide			
	$AcO(CH_2)_3X$	$Ac(CH_2)_3OH$	$AcOCH_2CH{=}CH_2$	O_2
Cl	0,62	0,27	0,05	0,14
Br	0,41	0,47	0,06	0,56
CN	0,18	0,58	0,04	–
SCN	0,74	0,18	0,03	0,13

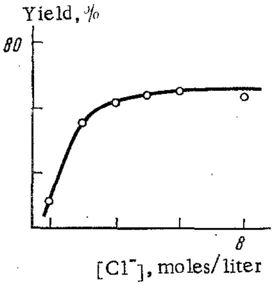


Fig. 3

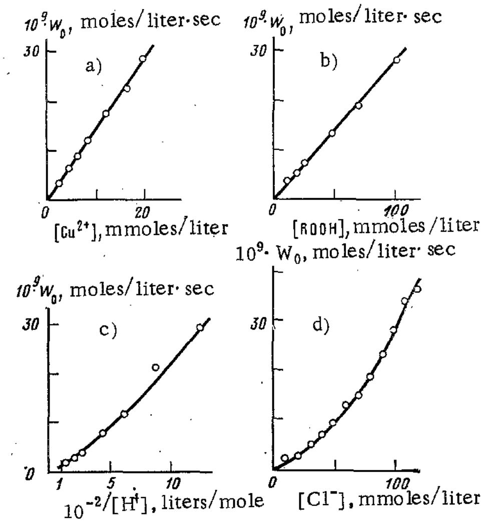


Fig. 4

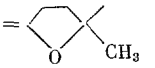
Fig. 3. Yield of 3-chloropropyl acetate as a function of Cl^- concentration in decomposition of 2-methyltetrahydro-2-furyl hydroperoxide. $[Cu^{2+}] = 100$ mmoles/liter; 20 ± 2°C.

Fig. 4. Initial rate of initiation of 2-methyltetrahydro-2-furyl hydroperoxide decomposition as a function of concentration, moles/liter: a) Cu^{2+} ([ROOH] = 0.1, $[Cl^-] = 0.1$, pH 3.00); b) ROOH ($[Cu^{2+}] = 0.02$, $[Cl^-] = 0.1$, pH 3.00); c) H^+ ([ROOH] = 0.1, $[Cu^{2+}] = 0.02$, $[Cl^-] = 0.1$); d) Cl^- ([ROOH] = 0.1, $[Cu^{2+}] = 0.02$, pH 3.00). [TNM] = $2\cdot10^{-3}$ mole/liter, $[C_2H_5OH] = 0.3$ mole/liter; 25°C.

It can be seen from Table 2 that the ligand environment of the copper ion has a substantial influence on the reaction product yields. Mixed complexes of Cu(II) probably decompose, generating peroxyl radicals

$$(ROOCu(II)X_n(H_2O)_{(5-n)})^{(1-n)+} \rightarrow ROO^\cdot + (Cu(I)X_n(H_2O)_{(4-n)})^{(1-n)+}.$$

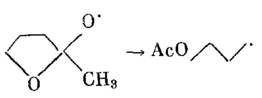
$n = 1—3$, R =



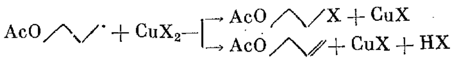
The peroxyl radicals are converted to alkoxyl radicals with the evolution of oxygen, in accordance with the reaction

$$2ROO^\cdot \rightarrow 2RO^\cdot + O_2$$

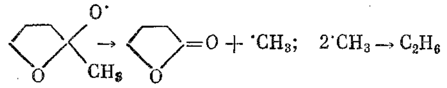
The alkoxyl radicals are for the most part isomerized with ring cleavage, giving 3-acetoxypropyl radicals



These latter radicals are oxidized by Cu(II) ions through a substitution or deprotonation mechanism



In the gas that is evolved, small quantities of ethanol are detected, in addition to the O_2. The formation of ethanol can be explained by fragmentation of the 2-methyltetrahydro-2-furyloxyl radical with elimination and subsequent dimerization of the methyl radicals



The oxygen that is formed as a result of the HP decomposition probably interacts not only with Cu(I)

$$2Cu^+ + 0.5O_2 + H_2O \rightarrow 2Cu^{2+} + 2OH^-$$

but also with other components of the reaction; and as a result, the O_2 yield is changed. In the course of the reactions under consideration here, the copper changes its valence repeatedly in alternating cycles, which makes it possible to carry out the decomposition of the HP in the presence of catalytic quantities of the salt. The formation of significant amounts of 3-acetopropanol (III) (see Table 2) cannot be explained solely by disproportionation of the radicals, since the yield of allyl acetate is far lower than the yield of the alcohol (III). The experimental conditions (low HP concentration) and the absence of any products of radical dehydrogenation enable us to eliminate the possibility that significant amounts of (III) are formed through abstraction of hydrogen by the 2-methyltetrahydro-2-furyloxyl radical. Also, we cannot postulate formation of (III) as a result of heterolysis of the O—O bond in the HP (I), since acidification of the $Cu(NO_3)_2$–HP (I)–H_2O–NaCl system stops the decomposition of the HP (I) as a result of decomposition of the peroxo complexes of Cu(II). With a further decrease in the pH, acid-catalyzed decomposition of the HP (I) takes place. The alcohol (III) is probably formed by reduction of the 2-methyltetrahydro-2-furyloxyl radical by the Cu(I) ion to the corresponding anion and capture of a proton by the anion, or the same anion may be formed by decomposition of the HP under the influence of Cu(I). However, we have not been able to find any indication in the literature that reactions of this sort actually take place. Finally, the alcohol (III) may be formed by reduction of the HP (I) by a complex of the Cu(II) with halide ions

$$ROOH + Cu(II) \rightarrow RO^- + HO^{\cdot} + Cu(III)$$

Actually, evidence in support of this view can be found in the favorable change of the ORP of the Cu(II)/Cu(III) pair as a result of the formation of stronger complexes of copper with the higher degree of oxidation. Moreover, the possibility of oxidation of chloro complexes of Cu(II) is supported by the decomposition, in the presence of these chloro complexes, of the water-soluble bis(2-methyltetrahydro-2-furyl) peroxide (IV) at 20°C

$$ROOR + Cu(II) \rightarrow RO^{\cdot} + RO^- + Cu(III)$$

The radicals in this reaction are registered through the decolorization of thionine and indigocarmine. With the aim of elucidating the nature of the radicals formed by HP decomposition under the influence of copper salts, we used TNM, which is an efficient acceptor of alkyl radicals [7]; the radicals interact with the TNM and are converted to the anion of nitroform (NF), which is registered quantitatively by spectrophotometry

$$R^{\cdot} + C(NO_2)_4 \rightarrow R^+ + C(NO_2)_3^- + NO_2^{\cdot}$$

or

$$R^{\cdot} + Cu(II) \rightarrow R^+ + Cu(I)$$
$$Cu(I) + C(NO_2)_4 \rightarrow Cu(II) + C(NO_2)_3^- + NO_2^{\cdot}$$

Since the rate of oxidation of Cu(I) by tetranitromethane ($K = 2 \cdot 10^8$ liters/mole·sec) [8] is considerably higher than the rate of oxidation under the influence of the HP

$$H_2O_2 + Cu(I) \xrightarrow{Cl^-} HO^{\cdot} + HO^- + Cu(II)$$

with $K = 4.9 \cdot 10$ [sic] liters/mole·sec [9], the HP decomposition is initiated only by the Cu(II).

The electron-acceptor radicals ($HO^{\cdot}$, $Cl^{\cdot}$) do not interact with TNM, and hence they cannot be detected directly by means of the TNM. It is known that $HO^{\cdot}$ destroys the NF that is the product of TNM conversion [10]. In order to suppress this process, we used C_2H_5OH as an inhibitor of the $HO^{\cdot}$

$$C_2H_5OH + HO^{\cdot} \rightarrow CH_3\dot{C}HOH + H_2O$$
$$C(NO_2)_4 + CH_3\dot{C}HOH \rightarrow C(NO_2)_3^- + CH_3CHO + NO_2 + H^+$$

The introduction of the alcohol into this system increases the rate of NF accumulation, which reaches its highest value with an alcohol concentration C = 300 mmoles/liter. This relationship indicates generation of $HO^{\cdot}$ or the radical $Cl^{\cdot}$, which is analogous in properties, formed through the reaction

$$HO^{\bullet} + Cl^{-} \rightleftarrows HO^{-} + Cl^{\bullet}$$

($K = 1.58 \cdot 10^7$ liters/mole·sec, pH 3) [11].

As would be expected, in the decomposition of the peroxide (IV) in the presence of TNM, the introduction of ethanol does not affect the initial initiation rate, since there are no $HO^{\bullet}$ radicals in the system. Increases of the TNM concentration in the range of 1-3 mmoles/liters, when C_2H_5OH is present, do not affect the rate of NF accumulation in decomposition of the HP (I); this indicates quantitative registration of all of the radicals that are formed. We determined the dependences of the initial initiation rate of the decomposition (W_i) of the HP (I) on the concentrations of HP, Cu(II), and Cl^-, and on the pH. As can be seen from Fig. 4, W_i is directly proportional to the concentrations of HP and Cu(II), and W_i varies in a complex manner with the Cl^- concentration

$$W_i = \frac{[Cu(II)]\,[ROOH]}{[H^+]} \cdot \{K_1[Cl^-] + K_2\,[Cl^-]^2 + K_3\,[Cl^-]^3\}$$

The complex power-function dependence of the reaction rate on the Cl^- concentration is explained by the formation of mixed complexes of the HP with chloro complexes of Cu(II) with the compositions $CuCl^+$, $CuCl_2$, and $CuCl_3^-$.

EXPERIMENTAL

The reaction products were analyzed by GLC in an LKhM-8MD-5 chromatograph with a flame-ionization detector in a stream of N_2 (25 ml/min), using control samples; the column (3 m × 3 mm) was packed with 10% PEGS on Chromosorb P or 15% Apiezon L on Chromaton N-AW-DMCS. The gas analysis was performed in an LKhM-8M chromatograph at ~ 20°C, katharometer, He carrier gas: columns 5% white mineral oil on Zikeev quarry tripoli (4 m × 3 mm), Porapac (2.7 m × 4 mm), and CaA zeolite (5 Å) (1 m × 3 mm). The PMR spectra were taken in a Tesla BS-467 spectrometer (60 MHz, CCl_4 solvent, TMS internal standard). The IR spectra were obtained in a UR-20 spectrophotometer in a thin layer. The pH values were measured with a glass electrode (pH-340 instrument) calibrated on standard buffer solutions. The values of pK_a for the HP (I) were determined spectrophotometrically (Specord UV-VIS instrument) by a procedure given in [12], (20 ± 0.05°C, at 250 nm, $\varepsilon_{ROOH} = 27.9$ liters/mole·cm (pH 6.86) and $\varepsilon_{ROO^-} = 291.2$ liters/mole·cm (0.4-1.0 M KOH solution). The pH was varied by adding KOH (cp grade). A constant ionic strength (0.10 mole/liter) was maintained with KCl (especially pure grade). The TNM was purified by a procedure given in [13]. Working solutions were prepared, taking aliquots of a freshly prepared saturated aqueous solution of TNM after acidification ($HClO_4$, cp grade) and filtration. The calculated quantity of Cu(II) salt solution was added to the TNM solution; the HP was added last. The concentration of TNM was found by reducing it to the NF by ascorbic acid. The rate of NF accumulation was determined spectrophotometrically (352 nm, $\varepsilon = 1.50 \cdot 10^4$ liters/mole·cm). The HP conversion in the kinetic measurements was no greater than 1%. The optical density of the solutions varied linearly with time; in the calculations, it was assumed to be proportional to the initial initiation rate. The $Cu(ClO_4)_2 \cdot 6H_2O$ was obtained by dissolving $(CuOH)_2CO_3$ (cp grade) in $HClO_4$ (cp grade). The copper salt solutions were filtered through a porous filter. The concentration of Cu(II) was determined by compleximetric titration, and the trace amounts of iron in the solutions were determined by atomic absorption (AAS-1 instrument).

For the $Cu(NO_3)_2$, the mole ratio Cu(II)/Fe(III) = $2 \cdot 10^4$. The organic peroxides were obtained by known methods. The H_2O_2 was purified by vacuum distillation.

Reaction of Hydroperoxide (I) with $CuCl_2$. To 100 ml of an aqueous solution containing 10 mmoles of $CuCl_2$ and an amount of NaCl sufficient to give a total concentration of Cl^- ion of 2-6 moles/liter (for Cl^- concentrations greater than 6, LiCl was used), there was added dropwise (1 h) 25 ml of 4 M aqueous solution (100 mmoles) of the HP (I), at 20 ± 2°C, and the mixture was stirred for 1 h additional. The gas that was evolved was collected in a gas burette. Then, the reaction mixture was extracted with ether (5 × 25 ml). A qualitative test for the presence of peroxide compounds was negative. The ether extracts were dried with $MgSO_4$, and the ether was driven off. The residue and the aqueous phase were analyzed separately.

Reaction of Hydroperoxide (I) with Cu(II) Ions in the Presence of Halides and Pseudo-Halides. To 100 ml of an aqueous solution containing 10 mmoles of $Cu(NO_3)_2$ and 400 mmoles of NaX (X = Cl, Br, CN, SCN), 25 ml of a 4 M aqueous solution (100 mmoles) of the HP (I) was added dropwise. The compounds 1-acetoxy-3-chloropropane, 1-acetoxy-3-bromopropane, and 4-acetoxybutyronitrile were isolated and identified by means of IR and PMR spectroscopy; the constants of these compounds match up with those reported in [14, 15, 16], respectively; also isolated was 1-acetoxy-3-thiocyanatropropane, bp 80-81°C (0.6 mm), n_D^{20} 1.4345. The IR spectrum of this last compound (ν, cm^{-1}): 1740 (O−C=O), 2160 (S−C≡N). PMR spectrum (δ, ppm): 1.98 s

(3 H, CH_3); 2.02 quint (2 H, CH_2, J = 6.5 Hz); 2.96 t (2 H, CH_2SCN, J = 6.5 Hz); 4.12 t (2 H, CH_2OAc, J = 6.0 Hz). Found: C 45.23, H 5.61, S 20.30, N 8.66%. $C_6H_6O_2NS$. Calculated: C 45.28, H 5.66, S 20.13, N 8.81%.

CONCLUSIONS

1. A method has been developed for generating free radicals by introducing salts containing complex-forming anions into a system consisting of Cu(II) aquo ions and a hydroperoxide. The radical nature of the reaction has been confirmed by the inhibitor method.

2. Data have been obtained indicating the formation of hydroxyl radicals in the decomposition of hydroperoxides under the influence of Cu(II) complexes.

3. Mixed complexes of Cu(II) with hydroperoxides in an aqueous medium are ionic in character, as indicated by results obtained in potentiometric measurements.

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DIRECT $^{13}C-^{13}C$ SPIN–SPIN COUPLING CONSTANTS OF OLEFINIC CARBONS IN VINYL ETHERS

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and B. A. Trofimov

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In the present work, we measured for the first time the direct $^{13}C-^{13}C$ SSCC of the olefinic carbons in the vinyl ethers (I)-(VI), with the aim of obtaining additional information on their structure:

$$\underset{\text{(I)—(VII)}}{CH_2{=}CH{-}OR}$$

$$R = Me(I),\ Et(II),\ n\text{-}Pr(III),\ n\text{-}Bu(IV),\ i\text{-}Pr(V),\ t\text{-}Bu(VI),\ Ph(VII).$$

Methyl vinyl ether (I) has been studied in the most detail. According to results obtained in most such studies, (I) exists in the form of two conformers; the s-cis conformer (Ia) is the more stable, whereas the second, less stable conformer is considered by some investigators to be the gauche form (Ib) and by other investigators to be the s-trans form (Ic) [1]:

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