Novel hydroperoxy sultam, 2-(6-bromo-pyrid-2-yl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazol-3-hydroperoxy 1,1-dioxide: synthesis, crystal structure and kinetics of catalytic interaction with cyclooctene†

O. Makota,*[a] A. Eilfeld,[b] Yu. Trach,[a] B. Schulze[b] and J. Sieler[c]

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The novel hydroperoxy sultam, 2-(6-bromo-pyrid-2-yl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazol-3-hydroperoxy 1,1-dioxide (HPS), was synthesized by the oxidation of the isothiazolium salt with hydrogen peroxide. As established by X-ray crystallography the unit cell of HPS in crystal state includes four molecules with a dimeric structure as a result of strong intermolecular hydrogen bond formation. The hydroperoxy sultam interacts with cyclooctene in the presence of molybdenum boride MoB as epoxidation catalyst at 40 °C. The additional consumption of HPS upon catalyst activation leads to an increase in the 1,2-epoxycyclooctane formation selectivity with increasing of HPS concentration. On the basis of the obtained results a kinetic reaction scheme was proposed. The equation for the reaction rate as well as the equation that connects the current concentration of hydroperoxide with reaction time and allows the calculation of the theoretical kinetic curves for HPS consumption were derived according to the kinetic scheme.

1. Introduction

Isothiazole derivatives are important organic substances since they express a broad range of biological activities. These compounds show anticonvulsant, sedative-hypnotic and antibacterial activities.[1–5] Isothiazolones are inhibitors of human leukocyte elastase.[6] Moreover, α-hydroperoxy sultams, which are the product of the isothiazolium salt oxidation reaction, also have great potential as novel chemoselective electrophilic oxidants. α-Hydroperoxy sultams oxidize secondary and tertiary amines to amine oxides, sulfides to sulfoxides and phoshines to phosphine oxides.[7,8] It is interesting to note that the oxidation reaction of hydroperoxy sultams with compounds containing heteroatom sulfur and a double bond led only to electrophilic attack at the sulfur atom but the double bond was not involved in the reaction. The reaction of hydroperoxy sultams with substances containing only one nucleophilic centre—the double bond—in this case with cyclooctene led to attack of the double bond with epoxide formation in the presence of an epoxidation catalyst.[9]

The selective oxidation of organic compounds is crucial in the chemical industry for the production of necessary oxygen containing compounds. However, the mechanism of this important process has not been established until now. Therefore it is difficult to influence this process purposefully. From this point of view it is necessary to study the kinetics of the oxidation reaction and the relationship between hydroperoxide structure and function.

The performance of hydroperoxy sultams as oxidation agents in oxidation reactions allows this process to be carried out at low temperatures. It is known that effective epoxidation agents at such temperatures are peroxy acids as a result of formation of inter- and mainly intramolecular hydrogen bonds.[10–12] Intramolecular hydrogen bonding is also the reason for the high epoxidation ability of some heterocyclic hydroperoxides, for example, cyclic α-azo-hydroperoxides.[8,13] One can expect that the high activity of hydroperoxy sultams also involves the formation of hydrogen bonds.

One might assume that the hydroperoxy sultam with a nitrogen atom in the aromatic ring attached to the nitrogen atom of the isothiazol ring can have a molecular structure in which an intramolecular hydrogen bond between the hydrogen atom of the peroxyl group and the nitrogen atom in the aromatic ring is formed and in such a way to promote oxygen transfer from the –OOH group to the double bond of the unsaturated compounds. Therefore it is possible to propose that this hydroperoxy sultam will be more active in catalytic interactions with unsaturated compounds.

Hence, in the present work, we report the synthesis of a novel hydroperoxy sultam with a nitrogen atom in the aromatic ring, 2-(6-bromo-pyrid-2-yl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazol-3-hydroperoxy 1,1-dioxide (HPS), its solid-state structure and kinetics of interaction with cyclooctene in the presence of molybdenum boride MoB—one of the molybdenum borides which are effective catalysts for the hydroperoxide epoxidation of unsaturated compounds.[14–19]

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[a] *Lviv Polytechnic National University, S. Bandera str. 12, U-79013 Lviv, Ukraine. E-mail: o_makota@polynet.lviv.ua*
[b] *Institute of Organic Chemistry, Leipzig University, Johannisallee 29, D-04103 Leipzig, Germany*
[c] *Institute of Inorganic Chemistry, Leipzig University, Johannisallee 29, D-04103 Leipzig, Germany*

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2. Experimental

2.1 General methods

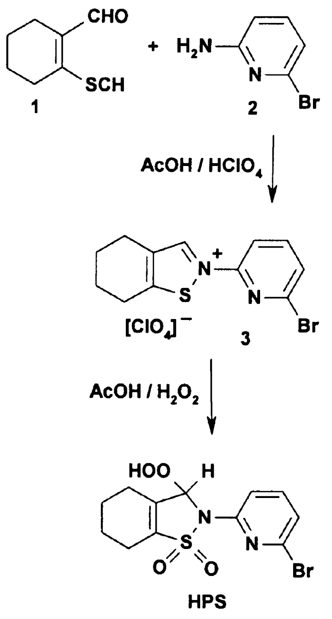
Melting point: Boetius micro-melting-point apparatus; corrected. UV/Vis spectra: Beckman DU-650; λ_{max} in nm (log ε). IR Spectra: Genesis FTIR Unicam Analytical System (ATI Mattson); KBr pellets; values in cm^{-1}. ^{1}H (200 or 300 MHz), ^{13}C (50 or 75 MHz) Spectra: Varian Gemini-200 and Varian Gemini-300 spectrometers; δ in ppm relative to Me$_4$Si as internal standard. HR-MS spectrum was recorded with a Bruker FT-ICR mass spectrometer apex II equipped with a 7 T magnet.

2.2 Synthesis

2.2.1 Procedure for the preparation of HPS. HPS was synthesized by the oxidation of isothiazolium salt **3** with 30% H_2O_2 in glacial acetic acid at room temperature (Scheme 1). The isothiazolium salt **3** was prepared by intramolecular cyclocondensation of β-thiocyanatovinyl aldehyde **1** and 2-amino-6-bromopyridine **2** in the presence of perchloric acid in glacial acetic acid as described in ref. 20.

2.2.2 Synthesis of 2-(6-bromo-pyrid-2-yl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazol-3-hydroperoxy 1,1-dioxide. H_2O_2 (0.7 ml; 30%) was added to a stirred suspension of **3** (0,26 mmol) in glacial acetic acid (0.7 ml) and stirring was continued at room temperature for 24 h. The solid product HPS was isolated by filtration and was recrystallized from ethanol. Yield 85%. White crystals; mp 149–153 °C.

The structure of HPS was established by IR, UV, NMR and HR-MS spectroscopy. IR (KBr): 1167 (SO_2, sym.), 1352 (SO_2, antisym.) cm^{-1}. UV (EtOH): λ_{max} (log ε) = 207.0 nm (4.23). ^{1}H NMR (acetone-d$_6$): δ ppm 1.85 (m, 4H, 2CH$_2$), 2.43 (m, 4H, 2CH$_2$), 6.61 (s, 1H, 3-H), 7.30 (d, J = 7.82 Hz, 1H, arom. H), 7.36 (d, J = 7.82 Hz, 1H, arom. H), 7.78 (t, J = 7.82 Hz, 1H, arom. H). ^{13}C NMR (acetone-d$_6$): δ ppm 18.9, 21.6, 21.8, 23.4, 89.2 (C1, see Fig. 1), 112.5 (C9), 123.8 (C11), 135.8 (C3), 140.2 (C2), 141.4 (C10), 141.7 (C12), 150.1 (C8). HR-MS (m/z): calculated (M$^{+\bullet}$) 360.98522, found 360.98536.



Scheme 1

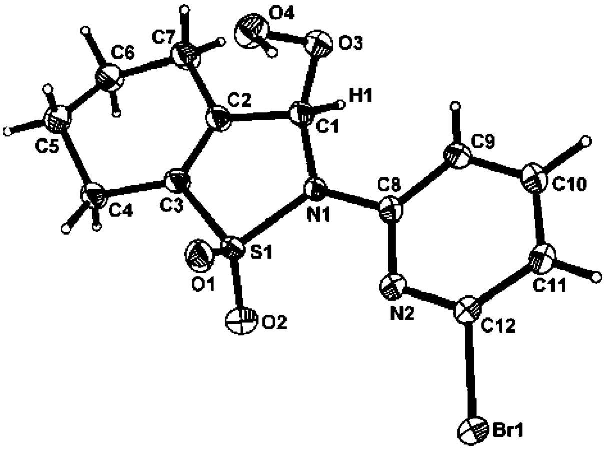


Fig. 1 ORTEP drawing of 2-(6-bromo-pyrid-2-yl)-2,3,4,5,6,7-hexahydro-1,2-benzisothiazol-3-hydroperoxy 1,1-dioxide (50% probability for thermal ellipsoids).

2.3 X-Ray crystal structure analysis

The crystals of HPS were obtained by crystallization from acetone. The intensities were measured on an IPDS2 diffractometer (Fa. STOE). The relevant crystallographic data are listed in Table 1. The structure was solved by direct methods and refined with SHELX-97.[21]

2.4 Kinetic measurements

The epoxidation reaction of cyclooctene with HPS was carried out in a thermostated glass reactor fitted with a reflux condenser under an argon atmosphere. The reaction mixture was

Table 1 Crystallographic data for HPS

Empirical formula	$C_{12}H_{13}N_2O_4BrS$
Formula weight	361.21
Temperature/K	213(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	8.8338(7)
b/Å	11.9410(6)
c/Å	12.9247(8)
α/°	90.00
β/°	97.45(1)
γ/°	90.00
Volume/Å^3	1351.82(15)
Z	4
Density/g cm^{-3}	1.775
Absorption coeff./mm^{-1}	3.210
Crystal size/mm	0.2 × 0.10 × 0.10
θ Range for data collection/°	2.6–29.0
Index ranges	$-11 \ll h \ll 11$ $0 \ll k \ll 15$ $0 \ll l \ll 17$
Reflections collected	3233
Independent reflections	2775 [R_{int} = 0.000]
Max./min. transmission	0.7396/0.5661
Data/parameters	2775/234
Goodness-of-Fit on F^2	1.139
Final R indices [$I > 2\sigma$ (I)]	R_1 = 0.0355, ωR_2 = 0.0994
R Indices (all data)	R_1 = 0.0435, ωR_2 = 0.1019
Lgst diff. peak, hole/e Å^{-3}	1.134, −0.725

stirred using a magnetic stirrer. For the kinetic measurements, the reactor was loaded with 0.01 g of catalyst, 0.3 ml of cyclooctene, 3.5 ml of chloroform as solvent and relevant amounts of HPS at a temperature 40 °C. It was established, in the absence of catalyst the decomposition of HPS under these reaction conditions did not proceed and 1,2-epoxycyclooctane (epoxide) was not formed. The kinetic curves of HPS nonproductive consumption were calculated at each moment of time as a difference between overall amount of HPS consumed and amount of HPS transformed into epoxide. The hydroperoxide content was determined by iodometric titration.[22] The rest of the components of the reaction mixture were analyzed by gas chromatography using a Hewlett Packard HP 6890 N, a capillary column DB-1 packed with dimethylsiloxane. The column temperature changed from 50 up to 250 °C with rate of 10 °C in 1 min.

3. Results and discussion

3.1 Description of HPS crystal structure

The molecular structure of HPS in the solid state revealed by X-ray crystallography is shown in Fig. 1. The bond parameters of the sultam ring for HPS are listed in Table 2. The C1–C2 bond length is equal to the value for a C(sp^2)–C(sp^2) single bond,[23] the C2–C3 bond length to a C(sp^2)–C(sp^2) double bond. The C1–N1–bond corresponds to a C(sp^2)–N single bond. The C3–S1 and the N1–S1 bonds also are typical values. The sultam ring is nearly exactly planar. The mean deviation from the least squares plane is 0.03 Å. The dihedral angle between the sultam ring and the pyridine ring is 6.1°. Therefore both rings are arranged in a nearly planar fashion.

In the crystal the unit cell of HPS includes four molecules which form dimeric structures as a result of strong intermolecular hydrogen bond formation between the atoms O4–H4···O1A and O4A–H4A···O1. The center of this dimeric structure is a symmetry center (Fig. 2). The bond parameters are: O4–H4 0.89(5) Å, H4–O1A 1.87(5) Å, O4–O1A 2.747(3) Å, O4–H4–O1A 170.0(4)°.

The results of the X-ray investigation also indicate that an O–H···N intramolecular hydrogen bond is not formed in this molecule of HPS. Hence, high activity of HPS at low temperatures is not connected with intramolecular hydrogen bonds.

Data about the relationship between the hydroperoxide structure and its activities in the oxidation reaction can be obtained when the kinetics of this reaction are studied in detail.

Table 2 Bond lengths (Å) and bond angles (°) of the isothiazole ring of HPS

C1–C2	1.502(4)	S1–O2	1.430(2)
C2–C3	1.326(4)	N1–C8	1.405(4)
C3–S1	1.745(2)	C2–C7	1.503(4)
S1–N1	1.672(2)	C3–C4	1.493(4)
N1–C1	1.459(4)	C1–H1	1.08(4)
S1–O1	1.435(2)	C1–O3	1.396(4)
C1–C2–C3	115.8(3)	S1–N1–C1	114.21(19)
C2–C3-S1	111.5(2)	N1–C1–C2	105.4(2)
C3–S1–N1	92.87(13)	O1–S1–O2	115.70(14)

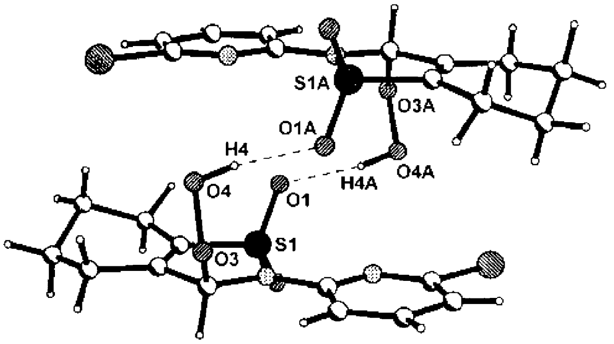


Fig. 2 The dimeric structure of HPS. (Symmetry code: A: 2 − x, 1 − y, −z.)

3.2 Kinetic studies

The investigation of the interaction process of cyclooctene with HPS in the presence of MoB demonstrated that the kinetic curves of HPS consumption have an induction period (Fig. 3) during the course of which the reaction rate increased.

It is likely that at the beginning of the epoxidation reaction the process of catalyst activation takes place, similar to the case of the reaction systems described in ref. 16–19.

The results of the catalytic epoxidation of cyclooctene with HPS at its initial amounts 0.005–0.04 mol l^{-1} are shown in Table 3. It is seen that the selectivity of 1,2-epoxycyclooctane formation in the epoxidation process increases with increasing HPS concentration in the reaction system.

This effect can be caused by the additional consumption of some amount of HPS upon catalyst activation. Fig. 4 shows the dependence of the amount of formed epoxide (ΔEP) on the amount of consumed hydroperoxide (ΔHPS). It can be seen that the dependence of ΔEP on ΔHPS is linear. This dependence did not begin at zero and crossed the x axis at a different initial concentration of HPS. It confirms the validity of our assumption about the additional consumption of some quantity of HPS upon catalyst activation. The value of selectivity of 1,2-epoxycyclooctane formation calculated from the tangent of the inclination angle of the line of ΔEP on ΔHPS dependence was 33%.

The initial rates of the catalytic consumption of HPS are determined by extrapolating the kinetic curve of hydroperoxide consumption on the activated catalyst after the induction period to the initial concentration of HPS under conditions corresponding to carrying out the process on completely activated catalyst at the beginning of the reaction (Fig. 3, line 4). Likewise, the initial rates of the catalytic consumption of HPS in the process of unproductive HPS decomposition (R_{do}) are determined by extrapolating the kinetic curve of unproductive hydroperoxide consumption on the activated catalyst. The initial rates of epoxide accumulation (R_{eo}) are determined analogously from the kinetic curves of epoxide formation.

Fig. 5 demonstrates the dependences of R_{do} and R_{eo} on the initial HPS concentration. As it shown the initial rate increase is not linear with increasing HPS concentration.

Based on the obtained results and our previous data[16–19] the investigated process can be described by a scheme which

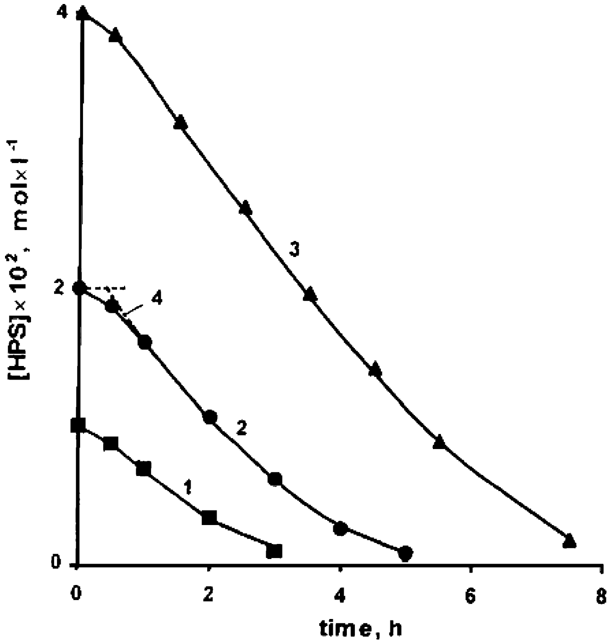


Fig. 3 The experimental points and theoretically calculated (using eqn (5)) kinetic curves for the consumption of HPS at different initial concentrations of hydroperoxide (1–3) as well as extrapolation of the kinetic curve after an induction period (4).

includes two consecutive reaction stages—catalyst activation and interaction of reactants on the activated catalyst.

The formation of complex (X_1) between initial catalyst (Cat) and HPS takes place at the first stage of the process:

$$\mathrm{Cat} + \mathrm{HPS} \overset{K}{\rightleftharpoons} X_1.$$

This complex decomposes and the activated form of the catalyst (Cat*) is formed:

$$X_1 \xrightarrow{k_a} \mathrm{Cat}^*.$$

Taking into account the above reaction scheme the rate of the activated catalyst formation is described by the equation:

$$\frac{\mathrm{d}[\mathrm{Cat}^*]}{\mathrm{d}t} = k_a K_1 [\mathrm{HPS}]_o \frac{[\mathrm{Cat}]_o - [\mathrm{Cat}^*]}{1 + K_1 [\mathrm{HPS}]_o} \qquad (1)$$

From Fig. 3 it is seen that the duration of the induction period does not depend on the initial concentration of HPS in the reaction system. Therefore, one may assume that $1 \ll K_1[\mathrm{HPS}]_o$. In this case eqn (1) takes the form:

$$\begin{aligned}\frac{\mathrm{d}[\mathrm{Cat}^*]}{\mathrm{d}t} &= k_a K_1 [\mathrm{HPS}]_o \frac{[\mathrm{Cat}]_o - [\mathrm{Cat}^*]}{K_1 [\mathrm{HPS}]_o} \\ &= k_a([\mathrm{Cat}]_o - [\mathrm{Cat}^*]) \qquad (2)\end{aligned}$$

Table 3 HPS conversion (Conv.) and selectivity (Sel.) of 1,2-epoxy-cyclooctane formation (with respect to consumed hydroperoxide) in the epoxidation reaction of cyclooctene with HPS catalyzed by MoB. The reaction time is 1 h

$[\mathrm{HPS}]_o \times 10^2$/mol l^{-1}	Conv. (%)	Sel. (%)
1	31	9
2	12	15
4	6	26

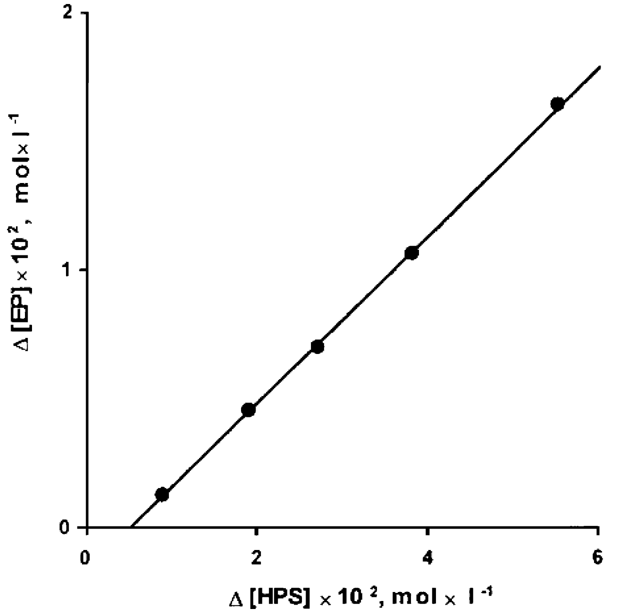


Fig. 4 Dependence of the amount of formed epoxide on the amount of consumed HPS.

Integrating eqn (2) gives the following expression for the concentration of the activated catalyst Cat*:

$$[\mathrm{Cat}^*] = [\mathrm{Cat}]_o(1 - \mathrm{e}^{-k_a t})$$

or

$$\frac{1}{k_a}\left(-\ln\frac{[\mathrm{Cat}]_o - [\mathrm{Cat}^*]}{[\mathrm{Cat}]_o}\right) = t$$

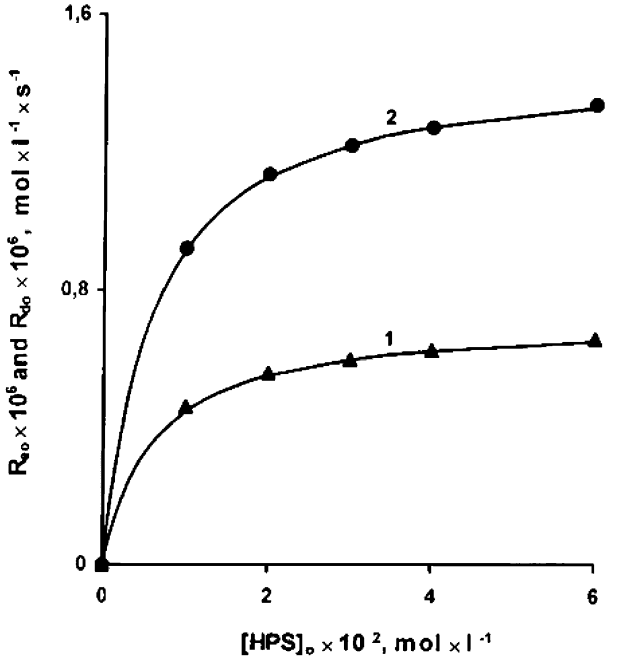


Fig. 5 Dependences of the initial rate of HPS consumption in both epoxidation (R_{eo}) (1) and decomposition (R_{do}) (2) reactions on the initial concentration of hydroperoxide.

The value of k_a has been found in two steps. In the first step we have assumed that in the moment of time t responsible for a point of crossing experimental (for example, Fig. 3, line 2) and extrapolated (for example, Fig. 3, line 4) curves:

$$\frac{[\mathrm{Cat}]_\mathrm{o} - [\mathrm{Cat}^*]}{[\mathrm{Cat}]^\mathrm{o}} = 0.05$$

The value of k_a calculated by this method is equal 6×10^{-4} s^{-1}. An improved value of $k_a = 8 \times 10^{-4}$ s^{-1} was evaluated from eqn (5), which is presented later, by the method of deflection minimization between the calculated and experimental curves.

After the induction period at the second stage of the reaction the process of HPS consumption proceeds on the activated catalyst as below.

The activated catalyst forms complex (X_2) with olefin (OL):

$$\mathrm{Cat}^* + \mathrm{OL} \overset{K_2}{\rightleftharpoons} \mathrm{X}_2;$$

the complex X_2 further reacts with HPS and complex (X_3) is formed:

$$\mathrm{X}_2 + \mathrm{HPS} \overset{K_3}{\rightleftharpoons} \mathrm{X}_3.$$

Moreover, the formation of complex (X_4) between activated catalyst and HPS takes place:

$$\mathrm{Cat}^* + \mathrm{HPS} \overset{K_4}{\rightleftharpoons} \mathrm{X}_4.$$

Based on this scheme in the second stage of reaction the amount of the activated catalyst which is not combined into complexes, can be presented as:

$$[\mathrm{Cat}^*] = \frac{[\mathrm{Cat}^*]_\mathrm{max}}{1 + K_2[\mathrm{OL}] + K_2K_3[\mathrm{OL}][\mathrm{HPS}] + K_4[\mathrm{HPS}]}$$

where $[\mathrm{Cat}^*]_\mathrm{max}$ is the maximum amount of activated catalyst, which is formed at the given moment of reaction.

The reaction products are formed in the following reactions:

$$\mathrm{X}_3 \xrightarrow{k_\mathrm{e}} \text{epoxidation products}$$

$$\mathrm{X}_4 \xrightarrow{k_\mathrm{d}} \text{decomposition products}$$

According to the above scheme in the second reaction stage the rates of epoxidation reaction (R_e) and reaction of HPS decomposition (R_d) are described by equations:

$$R_\mathrm{e} = \frac{k_\mathrm{e}K_2K_3[\mathrm{OL}][\mathrm{HPS}][\mathrm{Cat}^*]_\mathrm{max}}{1 + K_2[\mathrm{OL}] + K_2K_3[\mathrm{OL}][\mathrm{HPS}] + K_4[\mathrm{HPS}]}$$

and

$$R_\mathrm{d} = \frac{k_\mathrm{d}K_4[\mathrm{HPS}][\mathrm{Cat}^*]_\mathrm{max}}{1 + K_2[\mathrm{OL}] + K_2K_3[\mathrm{OL}][\mathrm{HPS}] + K_4[\mathrm{HPS}]}$$

The overall equation of the rate of hydroperoxide consumption (R) has the form:

$$\begin{aligned} R &= R_\mathrm{e} + R_\mathrm{d} \\ &= \frac{(k_\mathrm{e}K_2K_3[\mathrm{OL}] + k_\mathrm{d}K_4)[\mathrm{HPS}][\mathrm{Cat}^*]_\mathrm{max}}{1 + K_2[\mathrm{OL}] + K_2K_3[\mathrm{OL}][\mathrm{HPS}] + K_4[\mathrm{HPS}]} \end{aligned} \qquad (3)$$

Since the HPS concentration in the reaction system is very small we can assume that:

$$1 + K_2[\mathrm{OL}] + K_2K_3[\mathrm{OL}][\mathrm{HPS}] \gg K_4[\mathrm{HPS}]$$

In this case, eqn (3) can be written as follows:

$$R = \frac{k_\mathrm{e}K_2K_3[\mathrm{OL}] + k_\mathrm{d}K_4}{1 + K_2[\mathrm{OL}] + K_2K_3[\mathrm{OL}][\mathrm{HPS}]}[\mathrm{HPS}][\mathrm{Cat}^*]_\mathrm{max}$$

or

$$\begin{aligned} R &= R_\mathrm{e} + R_\mathrm{d} \\ &= \frac{k_\mathrm{e}K_\mathrm{e\cdot ef}[\mathrm{OL}][\mathrm{HPS}][\mathrm{Cat}^*]_\mathrm{max}}{1 + K_\mathrm{e\cdot ef}[\mathrm{OL}][\mathrm{HPS}]} \\ &\quad + \frac{k_\mathrm{d}K_\mathrm{d\cdot ef}[\mathrm{HPS}][\mathrm{Cat}^*]_\mathrm{max}}{1 + K_\mathrm{e\cdot ef}[\mathrm{OL}][\mathrm{HPS}]} \end{aligned} \qquad (4)$$

where $K_\mathrm{e\cdot ef}$ and $K_\mathrm{d\cdot ef}$ are effective constants of the epoxidation and decomposition processes:

$$K_\mathrm{e\cdot ef} = \frac{K_2K_3}{1 + K_2[\mathrm{OL}]} \quad \text{and} \quad K_\mathrm{d\cdot ef} = \frac{K_4}{1 + K_2[\mathrm{OL}]}.$$

After the induction period hydroperoxide consumption takes place on the fully activated catalyst and its amount is equal to the amount of the initial catalyst $[\mathrm{Cat}^*]_\mathrm{max} = [\mathrm{Cat}]_\mathrm{o}$.

According to eqn (4) the linear dependences of the initial rate of the epoxidation reaction and the rate of HPS decomposition on the initial HPS concentrations have to observe in

$$\frac{1}{R_\mathrm{eo}} = \mathrm{f}\frac{1}{[\mathrm{HPS}]_\mathrm{o}} \quad \text{and} \quad \frac{1}{R_\mathrm{do}} = \mathrm{f}\frac{1}{[\mathrm{HPS}]_\mathrm{o}} \quad \text{coordinates :}$$

$$\frac{1}{R_\mathrm{eo}} = \frac{1}{k_\mathrm{e}[\mathrm{Cat}]_\mathrm{o}} + \frac{1}{k_\mathrm{e}K_\mathrm{e\cdot ef}[\mathrm{OL}]_\mathrm{o}[\mathrm{Cat}]_\mathrm{o}} \times \frac{1}{[\mathrm{HPS}]_\mathrm{o}}$$

and

$$\frac{1}{R_\mathrm{do}} = \frac{K_\mathrm{e\cdot ef}[\mathrm{OL}]_\mathrm{o}}{k_\mathrm{d}K_\mathrm{d\cdot ef}[\mathrm{Cat}]_\mathrm{o}} + \frac{1}{k_\mathrm{d}K_\mathrm{d\cdot ef}[\mathrm{Cat}]_\mathrm{o}} \times \frac{1}{[\mathrm{HPS}]_\mathrm{o}}$$

As can be seen from Fig. 6 these dependences are linear and it allows us to calculate k_e, $K_\mathrm{e\cdot ef}$ and $k_\mathrm{d}K_\mathrm{d\cdot ef}$. The following values of these parameters were found: $k_\mathrm{e} = 2.8 \times 10^{-7}$ mol g^{-1} s^{-1}; $K_\mathrm{e\cdot ef} = 280$ l^2 mol^{-2}; $k_\mathrm{d}K_\mathrm{d\cdot ef} = 9.6 \times 10^{-5}$ l g^{-1} s^{-1}.

Taking into consideration the first and the second stages of the process the rate equation for HPS consumption during the entire period of reaction can be expressed as follows:

$$-\frac{\mathrm{d}[\mathrm{HPS}]}{\mathrm{d}t} = \frac{k_\mathrm{e}K_\mathrm{e\cdot ef}[\mathrm{OL}] + k_\mathrm{d}K_\mathrm{d\cdot ef}}{1 + K_\mathrm{e\cdot ef}[\mathrm{OL}][\mathrm{HPS}]}[\mathrm{HPS}][\mathrm{Cat}]_\mathrm{o}(1 - \mathrm{e}^{-k_\mathrm{a}t})$$

The integral form of this equation can be written as:

$$\frac{1}{A}\ln\frac{[\mathrm{HPS}]_\mathrm{o}}{[\mathrm{HPS}]} + \frac{B}{A}([\mathrm{HPS}]_\mathrm{o} - [\mathrm{HPS}]) = t - \frac{1}{k_\mathrm{a}}(1 - \mathrm{e}^{-k_\mathrm{a}t}) \qquad (5)$$

where

$$A = (k_\mathrm{e}K_\mathrm{e\cdot ef}[\mathrm{OL}] + k_\mathrm{d}K_\mathrm{d\cdot ef})[\mathrm{Cat}]_\mathrm{o};\ B = K_\mathrm{e\cdot ef}[\mathrm{OL}]$$

The theoretical kinetic curves for the consumption of HPS over time evaluated from eqn (5) with the use of parameters determined from the dependences of the initial reaction rates (R_o, R_eo, R_do) on the initial HPS concentration, virtually coincide with the experimental curves (Fig. 3), which may be evidence for the validity of the assumed model for the reaction

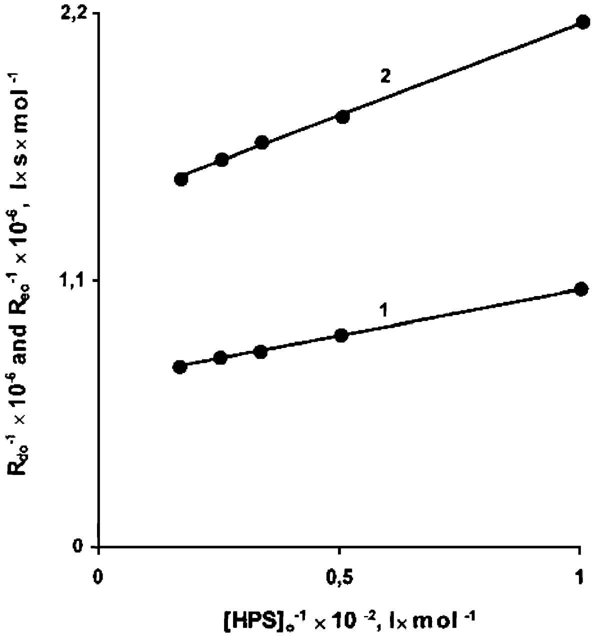


Fig. 6 Dependences of $1/R_{do}$ (1) and $1/R_{eo}$ (2) *vs.* $1/[HPS]_o$.

of the epoxidation of cyclooctene by HPS in the presence of MoB.

Comparison of the obtained kinetic results for the catalytic interaction of HPS with cyclooctene with the results of kinetic investigations into the catalytic interaction of a better studied hydroperoxide [*tert*-butyl hydroperoxide (TBHP)], with unsaturated compounds allows us to make the following conclusions.

HPS formed a more stable catalyst–hydroperoxide complex than TBHP. This is evident from a comparison of dependences of reaction rate on hydroperoxide concentration. In the case of TBHP the reaction is first order with respect to hydroperoxide up to a TBHP concentration of 1 mol l^{-1}.[16,17] In the case of HPS at concentrations 10 times lower the reaction order is less than first order with respect to hydroperoxide. The higher stability of the catalyst–hydroperoxide complex and accordingly the higher value of the equilibrium constant K_4, leads to an increase in the rate of the hydroperoxide decomposition process (R_d, eqn (4)). It results in a lower selectivity of the epoxidation process in the presence of hydroperoxide with more complex formation ability (HPS). In the case of TBHP the selectivity is more than 95%.

It is not necessarily so that the structure of the compound in solution will be the same as in the crystal. However, taking into account the high activity of HPS it is possible to assume that HPS also contains intermolecular hydrogen bonds in solution. If in the case of TBHP intermolecular hydrogen bonds are formed between the hydrogen atom of the peroxyl group of one hydroperoxide molecule and the oxygen atom of the peroxyl group of another molecule[24], then in the case of HPS intermolecular hydrogen bonds are formed between the hydrogen atom of the peroxyl group of one hydroperoxide molecule and the oxygen atom of the non-peroxyl group of another molecule. This intermolecular hydrogen bond probably is more favourable to stabilization of the intermediate state of the epoxidation reaction and leads to a decreasing in O–H and O–O peroxyl group bond energy. This could explain why the oxidation reaction proceeds in the presence of HPS at lower temperatures than in the presence of TBHP.

An additional fact that influences the high HPS activity is the structure of its molecule. The HPS molecule contains nitrogen, sulfur, non-hydroperoxide oxygen and bromine atoms which increase the electrophilic character of the peroxyl oxygen atom and in such a way stabilize an intermediate cyclooctene–catalyst–hydroperoxide complex responsible for epoxide formation.

4. Conclusions

2-(6-Bromo-pyridyl)-2,3,4,5,6,7-hexahydro-1,2-benzisothia-zol-3-hydroperoxy 1,1-dioxide was prepared by the oxidation of the isothiazolium salt with hydrogen peroxide at room temperature. It was established by X-ray analysis that in the crystal HPS molecules are in a dimeric form as a result of intermolecular hydrogen bond formation.

It was shown that the reaction of hydroperoxy sultam with cyclooctene in the presence of a catalyst leads to epoxide formation. At the beginning of this reaction catalyst activation takes place and some quantity of hydroperoxide is consumed. As a result, the 1,2-epoxycyclooctane formation selectivity depends on the initial concentration of HPS—increasing HPS concentration leads to an increase in the selectivity.

The kinetic regularities of the interaction of HPS with cyclooctene in the presence of MoB were studied. On the basis of the obtained results a kinetic scheme was proposed and the kinetic parameters of the process were calculated. The equation for the reaction rate and the equation that connected the current concentrations of hydroperoxide with reaction time were derived according to the kinetic scheme.

Further investigations will be focused on studying the intermediate structures proposed in the kinetic scheme.

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