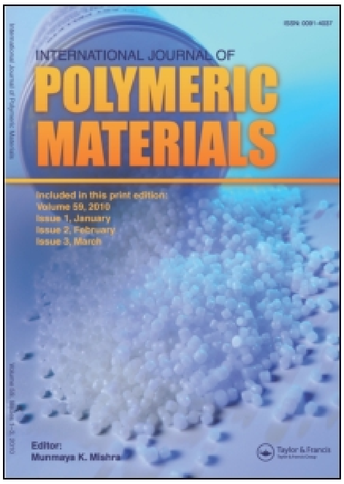

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Kinetics and Mechanism of Oxidation of Mono- and Polyacetals

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Kinetics and Mechanism of Oxidation of Mono- and Polyacetals

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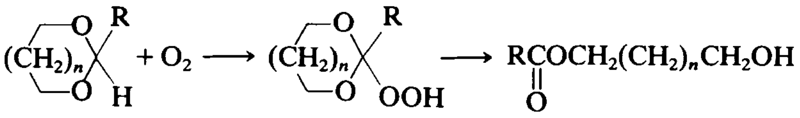
Kinetics and mechanisms of oxidation of 6 acetals by molecular oxygen and ozone in liquid phase have been studied. Reaction with molecular oxygen (70°C, 15–16 hr) leads to the formation monoethers of the corresponding glycols with 68–90% selectivity. Salts of metals and complexes with crown-ethers have increased the reaction rate significally. Ozone have reacted with acetals with formation similar products. The mechanisms of intermediate stages have been proposed.

KEYWORDS: Oxidation, polyacetals, kinetics, mechanism, hydroperoxides, crown-ethers

Oxidation of 1,3-dioxacyclanes and 1,1-dialkoxyalkanes with molecular oxygen leads to the corresponding hydroperoxides.[1–4] At the acetal conversion of 5...15% the yield of the hydroperoxides (AOOH) makes up 100...80% of the absorbed O_2 quantity (Table I). With AH conversion increase (20...35%) the selectivity over AOOH falls to 50...40%. With the temperature rise from 70°C to 120°C the percentage of AOOH decreases, and at a temperature of more than 100°C the main products are the corresponding monoesters of glycols, the percentage of which in the reaction mixture achieves 70...90% when the substrate conversion makes up 50...80%.



$n = 0, 1 \qquad R = H, CH_3$

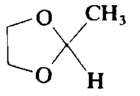
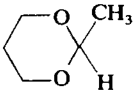
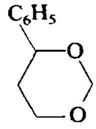
Initiated oxidation of acetals (AH) proceeds according to the radical chain mechanism,[7–8] and the rate of the interaction is described in the following formula

$$W = (k_2/\sqrt{k_6})[AH]\sqrt{Wi}$$

When oxidation of acetals proceeds in the presence of initiators maintaining the constant rate of the generation of radicals, and with a sufficiently high concentration of oxygen, the controlling step of chain continuation is a reaction of $AO_2^{\cdot}$ with AH. In acetal molecules there are two reaction centers of the C—H bond adjacent to two oxygen atoms and to one atom. In order to estimate a contribution of each bond to the reaction of chain continuation, the kinetic

TABLE I

Kinetics of the oxygen absorption and of the accumulation of hydroperoxides (AOOH) and esters (EOH) in oxidation of acetals (AH) (70°C, AIBN)[5,6]

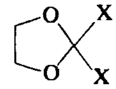
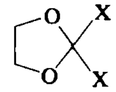
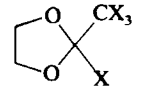
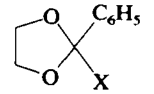
Concentration, mole/l				
Absorbed O_2	Formed AOOH	Formed EOH	Conversion AH, %	Selectivity over AOOH, %
	$[AOOH]_0 = 0.07$ mole/l, $[AH]_0 = 11.2$ mole/l, 50°C			
0.30	0.30	—	2.0	100
0.48	0.50	—	5.0	100
1.08	1.0	0.06	10	93
1.64	1.40	0.10	14	87
	$[AH]_0 = 9.5$ mole/l, $[AIBN]_0 = 1.0 \cdot 10^{-2}$ mole/l			
0.39	0.36	0.02	4	100
0.58	0.48	0.08	6	83
0.78	0.62	0.14	8	80
1.00	0.74	0.24	10	74
1.11	0.78	0.30	12	71
	$[AH]_0 = 6.8$ mole/l, $[AIBN]_0 = 1 \cdot 10^{-2}$ mole/l			
0.47	0.39	0.06	7	83
0.77	0.63	0.12	11	80
1.00	0.76	0.21	15	76
1.41	0.99	0.40	10	71
$CH_3CH(OC_2H_5)_2$	$[AH]_0 = 7.4$ mole/l, $[AIBN]_0 = 3 \cdot 10^{-2}$ mole/l			
0.16	0.15	—	2	94
0.31	0.29	0.01	4	94
0.60	0.49	0.01	8	82
1.00	0.62	0.35	13.5	60
1.78	0.70	1.05	24	39

isotope effect (KIE) and the reaction with cumylperoxyradicals were investigated. The substitution of acetal carbon hydrogen atoms for heavier isotope (deuterium) leads to the decrease in O_2 absorption rate, and consequently, to the decrease in parameters $k_2 \cdot k_6^{-1/2}$, i.e. it leads to the manifestation of KIE (Table II).

KIE value obtained (KIE = 2.0–4.1) testifies, mainly, to the fact of a peroxide radical attack of the C—H bonds adjacent to two oxygen atoms; the increase in KIE value in the transference from the formales to the derivatives of ethyl aldehyde, and, especially, to those of benzaldehyde, is partially connected with the increase in selectivity of a radical $AO_2^{\cdot}$ attack of the C—H bond.

TABLE II

Oxidation of acetals and deuterium derivatives with molecular oxygen ($70°C$; $[AH] = 1.9 \div 3.9$ mole/l; $V_i = (1.1\text{–}6.2) \cdot 10^7$ mol/l s)[9]

Compound	oxidizability of acetals $(k_2 \cdot k_6^{-1/2}) \cdot 10^4)$ l/mole s$)^{1/2}$		
	$x = H$	$x = D$	$KIE = \frac{k_H}{k_D}$
$CX_2(OC_3H_7)_2$	8.1	4.0	2.0
	10.4[a]	4.7	2.2
	11.1	4.6	2.4
$CX_3CX(OC_3H_7)_2$	22.4	11.5	2.4
	63.6	20.5	3.1
	212.0	52.0	4.1

[a] 50°C.

An opportunity of acetal oxidation acceleration in the presence of catalytic quantities of salts of metals of variable valency (Fe(III), Ni(II), Co(II), Cr(III)) was studied by the example of 1,3-dioxolane (Table III).[11,12]

The kinetic curves of the oxygen absorption in the catalytic oxidation of acetals possess an accelerated character. At the initial state of oxidation, when

TABLE III

Influence of salt nature upon the maximum (V_{O_2}) and relative ($V_{rel.}$) rate of oxidation of 1,3-dioxolane in a chlorobenzole solution (40°C, $[AH] = 2.4$, $[MeX_n] = 5 \cdot 10$ mole/l [12])

Salt (MeX)	$V_{O_2}^{max} \cdot 10^6$ mole/l s	$V_{rel.}$[a]	Salt (MeX)	$V_{O_2}^{max} \cdot 10^6$ mole/l s	$V_{rel.}$[a]
$Fe(C_{13}H_{31}COO)_3$	0.8	1.0	$Co(acac)_2$	80	100
$Cr(C_3H_7COO)_2$	0.07	0.1	$Co(CH_3COO)_2$	525	657
$Fe(C_{17}H_{35}COO)_2$	0.9	1.11	$Co(iso\text{-}C_4H_9COO)_2$	133	166
$Fe(C_6H_5COO)_3$	2.1	2.6	$Co(C_4H_9COO)_2$	190	248
$Cr(C_{17}H_{35}COO)_3$	2.8	3.5	$Co(C_9H_{19}COO)_2$	240	300
$CoCl_2 \cdot 2DHSO$	3.4	4.2	$Co(C_{17}H_{35}COO)_2$	315	394
$Ni(acac)_2$	3.8	4.7	$Co(C_{17}H_{35}COO)_2$	164	205

[a] $V_{rel.} = V_{O_2}^{max} / V_{O_2}^{max}$ $Fe(C_{15}H_{31}COO)_2$

concentration of the hydroperoxide has low value ([AOOH] $\ll 1 \cdot 10^{-2}$ mole/l), the process may be characterized by the initial rate $V_{O_2}^0$. With the increase in AOOH content in the reaction mixture the initial rate of the acetal oxidation goes up and achieves the maximum value $V_{O_2}^{max}$, which keeps for an undefinite period of time. Then the process is retarded, the oxygen absorption completion is accompanied by the precipitation of a catalyst. The rate of the 1,3-dioxolane oxidation in the presence of palmitate of Fe(III), which is equal in its value to that of the initiated ([AIBN] $= 5 \cdot 10^{-3}$ mole/l) oxidation, is taken as a unit conventionally. The activity of the salts tested goes up in the series Fe(III) < Cr(III) < Ni(II) ≪ Co(II)[13] when the oxidation of 1,3-dioxolane in a chlorobenzole solution takes place; the maximum accelerating action, characteristic of Co(II) palmitate, makes up ~394 times, and that of Co(II) acetate achieves 657 times. An introduction of Cr(II) salt into the system leads to the considerable decrease in the rate of the oxidation.[13] In oxidation of pure 1,3-dioxolane (14.3 mole/l) the activity of the salts changes: Fe(III) < Ni(II) < Cr(III) < Co(II), the maximum accelerating action is achieved with $Co(C_7H_{15}COO)_2$ and makes up ~28 times (the rate of the oxidation of Fe(II) benzoate is equal in its value to that of the initiated 1,3-dioxolane, is taken as a unit) (Table IV). The rate of acetal oxidation is determined by a cycle size and by a substituent nature of the acetal carbon atom (Table V).

Depending on a cycle size the rate of the oxidation goes up in the following way: 1,3-dioxepane < 1,3-dioxepane < 1,3-dioxolane. For the 2-alkyl-1,3-dioxolane the rate of the oxidation increases in the series of the substituents: methyl < isopropyl < phenyl.[13]

Cobalt salts possess a regulating function,[16] and depending on the nature of the anion, provide practically quantitative formation either of the hydroperoxide of the absorbed oxygen, or of the glycol monoester, when conversion of the 1,3-dioxolane is less than 20%.

During the work[17] it has been found that the introduction of crown-ether into the oxidizable system considerably increase the rate and selectivity of the process as well as the substrate conversion (Table VI).

When the 1,3-dioxolane oxidation is carried out in the absence of a crown-ether the reaction is practically arrested and AH conversion does not exceed 1%.

The crown-effect achieves its maximum value with introduction of dibenz-18-

TABLE IV

Influence of salt nature upon the maximum ($V_{O_2}^{max}$) and relative ($V_{rel.}$) rate of oxidation of pure 1,3-dioxolane[12] (40°C, [AH] = 14.3, $[MeX_n] = 5 \cdot 10^{-3}$ mole/l)

Salt (MeX_n)	$V_{O_2}^{max}$ 10^5 mole/l s	$V_{rel.}$[a]	Salt (MeX_n)	$V_{O_2}^{max}$ 10^5 mole/l s	$V_{rel.}$[a]
$Fe(C_6H_5COO)_3$	0.5	1	$Co(C_3H_7COO)_2$	12.5	25.0
$Ni(acac)_2$	2.1	4.2	$Co(C_4H_9COO)_2$	13.8	27.0
$CrCl_3$	7.4	14.8	$Co(C_7H_{15}COO)_2$	14.0	28.0
$CoCl_2$	16.4	32.8	$Co(C_9H_{19}COO)_2$	9.9	19.8

[a] $V_{rel.} = V_{O_2}^{max} / V_{O_2}^{max}$ $Fe(C_6H_5COO)_3$

TABLE V

Influence of acetal structure upon the maximum ($V_{O_2}^{max}$) relative (V_{rel}) rate of oxidation (40°C; [AH] = 2.4 [$Co(C_{15}H_{31}COO)_2$] = 5 · 10^{-3} mole/l)[13–15]

Acetal	$V_{O_2}^{max}$ 10^4 mole/l s	$V_{rel.}$[a]	Acetal	$V_{O_2}^{max}$ 10^4 mole/l s	$V_{rel.}$[a]
$H_2COC(CH_3)_2CH_2CH_2O$	0.01	1	$CH_3HCOCH_2CH_2CH_2O$	0.05	5
$H_2COCH_2CH_2CH_2CH_2O$	0.33	33	$C_3H_7HCOCH_2CH_2CH_2O$	0.05	5
$H_2COCH_2CH_2O$	3.2	320	$CH_3HCOCH_2CH_2O$	3.4	340
iso-$C_3H_7HCOCH_2CH_2O$	3.0	300	$C_6H_5HCOCH_2CH_2O$		

[a] $V_{rel.} = V_{O_2}^{max}/V_{O_2}^{max}$ [4,4-dimethyl-1,3-dioxane].

crown-6 into the system. In the presence of 18-crown-6 the oxidation of 1,3-dioxolane leads, chiefly, to monoformiate ethylenglycol.

In the works[18–21] the kinetics and mechanism of 1,3-dioxacyclanes have been investigated. It has been established that the reaction is of a first order as to the substrate, i.e. ozonation is a bimolecular reaction.

$$AH + O_3 \rightarrow AOOOH \rightarrow \text{the products of the reaction}$$

According to the scheme offered by Deslongchamps,[18] in the state of transition of acetals with ozone a positive charge, stabilized by the corresponding position of the orbitals of the free electron pairs of oxygen atoms, is formed on the carbon atom of an acetal group. The forming labile α-oxyacetal and hydrotrioxide decompose giving an ester and alcohol. The first spectroscopic proofs of the hydroperoxide formation (AHOOH)-labile products of acetal ozonation were obtained in the investigation of linear acetals of acetic and cyclic acetals of benzaldehyde.[37,38] In the works[21,22] the synthesis conditions, kinetics and products of the thermal decomposition and some reactions of hydrotrioxides of cyclic and linear acetals of formaldehyde, ethyl aldehyde and benzaldehyde, has been investigated. In the work[22] it has been established that at ozonation of the

TABLE VI

Influence of the crown-ether (ce) nature upon the rate of oxidation ($V_{O_2}^{max}$), concentration of the absorbed oxygen [O_2], maximum concentration of the hydroperoxide [AOOH], selectivity of AOOH formation (S_{AOOH}), conversion of the 1,3-dioxolane (K_{AH})[17] (40°C; [AH] = 14.3, [$(C_9H_{19}COO)_1Co$] = 5 · 10^{-3} mole/l)

Crown-ether	Duration, hr.	$V_{O_2}^{max}$ 10^5 mole/l s	[O_2] mole/l	[AOOH] mole/l	S_{AOOH}	K_{AH}, % mole
—	3	1.7	0.1	0.1	100	0.7
15-crown-5	8	1.1	0.4	0.2	50	2.0
Dicyclohexyl-18-crown-6	33	3.1	1.5	1.2	80	10.5
18-crown-6	33	5.6	2.7	0.9	33	19
Dibenz-18-crown-6	14	12.4	3.0	2.8	93	21

TABLE VII

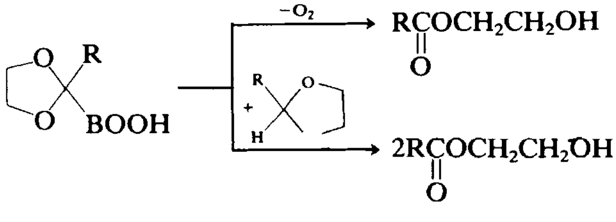
Influence of the acetal structure and concentration upon the yield of monoethers (−60°C, reaction volume 1 ml)

Acetal, mmol				
Taken	Having taken part in the reaction	Ozon having taken part in the reaction, mmol	Monoether formed, mmol	[Monoether] / [ozon]
		1,3-dioxolane		
14.3	1.5	0.7	1.4	2.0
14.3	2.3	1.0	1.9	1.9
4.8[a]	1.3	1.2	1.2	1.0
3.6[a]	1.6	1.3	1.4	1.0
		2-methyl-1,3-dioxolane		
11.2	1.5	0.9	1.5	1.9
11.2	1.8	0.8	1.6	2.0
3.7[a]	1.8	1.0	1.8	1.8
		2-isopropyl-1,3-dioxolane		
8.1	1.7	0.8	1.6	2.0
8.1	3.2	1.8	3.0	1.7
		2-phenyl-1,3-dioxolane		
7.4	1.3	0.6	1.3	2.0
7.4	2.4	1.2	2.4	2.0
3.7[a]	0.7	0.5	0.7	1.4
1.9[a]	0.8	0.6	0.7	1.1

[a] Solvent—ethylacetate.

1,3-dioxolane, 2-methyl-1,3-dioxolane, 2-isopryl-1,3-dioxolane and 2-phenyl-1,3-dioxane (−60°C) without a solvent and highly concentrated solutions 1.5 . . . 2 mole of the substrate is consumed for 1 mole of ozone having taken part in the reaction (Table VIII).

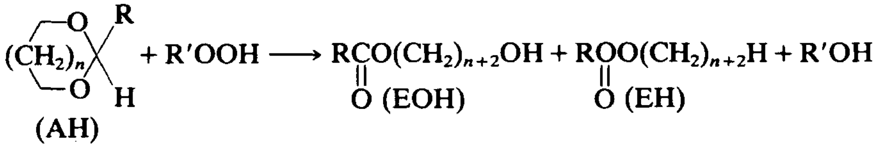
These results are obviously connected with the fact that in concentrated (7 . . . 14 mole/g) acetal solutions hydrotrioxides oxidize the substrate simultaneously with a monomolecular decomposition.



$R = H, CH_3, CH(CH_3)_2, C_6H_5$

With small concentrations of acetal the main way of the product formation is a monomolecular decomposition of hydroperoxide. High concentration of acetals in the system promotes, mainly, a biomolecular reaction which leads to the increase in the yield of the monoesters of the ozon having taken part in the reaction.[23]

Thermal decomposition of the organic hydroperoxides (ROOH) in the medium of 1,3-dioxacyclanes in the interval of 80 . . . 130°C leads to the formation of the monoesters of glycol (EOH), esters (EH) and corresponding hydroperoxides of alcohols (R'OH)[6,24–27]



The formation of the ester (EH) and monoester of glycol is explained by the parallel reactions[24]

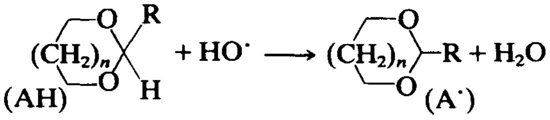
$$E^{\cdot} + AH \rightarrow EH + A^{\cdot}$$
$$E^{\cdot} + R'OOH \rightarrow EH + R'O^{\cdot}$$
$$R' = C_6H_5CH(CH_3)_2, \quad (CH_3)_3C$$

The investigation of the conditions of the process (temperature, nature and ratio of the reagents) upon the yield of monoesters of glycol testifies to the fact of various efficiency of the hydroxylating action of the hydroperoxides. When hydroperoxide of tret-butyl (HPTB) is used, the yield of monoesters from 2-alkyl-1,3-dioxolanes changes from 72% to 83%, and the yield of monoesters from 1,3-dioxanes makes up 70 . . . 72%. The conversion of the acetal changes in the interval of 4 . . . 12%. The yield of monoesters from the consumed hydroperoxide of cumene (HPC) from 2-alkyl-1,3-dioxolanes makes up 60 . . . 90%, and that from 2-methyl-1,3-dioxolanes achieves 90%. Irrespective of the structure of the hydroperoxide (HPTB, HPK) the yield of monoester in hydroxylation of 1,3-dioxolane is rather low (38 . . . 40%).[25,26] The products of the thermal transformation of the hydroperoxides—the corresponding alcohols accumulating in the reaction mixture, hinder the isolation of the main products. Application of cyclic acetals of the own hydroperoxides (AOOH) in hydroxylation allows to avoid these complications and to achieve high yields of monoesters from the hydroperoxide taken, which may be explained by the identity of the products of transformation AH and decomposition AOOH.[27]

It has been established that the 1,3-dioxolane oxidation with hydrogen peroxide in the temperature interval of 80 . . . 120°C also leads to the formation of monoesters of glycol the yield of which is maximum at 80°C on an oxidant basis and is weakly dependent on the substituent structurre in the second position and on the cycle size.

According to the well-known notion about homolytical transformation of cyclic acetals[28] the mechanism of the reaction may be represented in the following way:

$$H_2O_2 \rightarrow 2HO^{\cdot}$$



$$A^{\cdot} + H_2O_2 \rightarrow {}^{\cdot}OH + AOH \rightarrow EOH$$

$A^{\cdot} + A^{\cdot} \rightarrow$ products of chain termination

Cyclic radicals due to their high nucleophility quickly react with H_2O_2 over oxygen–oxygen bond, which leads to the formation of labile 2-oxiderivatives isomerizing into monoesters EOH. The chain termination proceeds, obviously on carbon-centered radicals $A^{\cdot}$, and at more than 100°C the process takes place on isomeric to them linear radicals $RC(O)O(CH_2)_{n+1}{}^{\cdot}CH_2$.[28] A decrease in the selectivity of the monoester formation with a temperature increase testifies indirectly to the fact that the role of mono- and biomolecular reactions of radicals $A^{\cdot}$, in which molecules H_2O_2 do not take part, grows.

Monoesters of glycol were obtained by way of oxidation of cyclic acetals with oxygen, hydroperoxides, ozon.

It has been established that oxidation of 1,3-dioxolanes and 1,3-dioxanes (70°C, duration 15–16 hr., conversion of acetals 45–78%) with molecular oxygen leads to the formation of monoesters of ethylene- and propylenglycol in 68–90% selectivity. Addition of salts of metals of variable valency and of crown-ether considerably increase the rate of oxidation (40–60°C, duration 2–8 hr., monoester yield 74–98% at the substrate conversion 13–20%). The decomposition of hydroperoxides in the medium of cyclic acetals (90–130°C, 3–5 hr., permits to produce monoesters in 76–94% yield from the transformed substrate at its conversion 10–90%. The most effective oxidant is ozon (1,3-dioxolanes, −60°C, 20–45 min, conversion 20–32%, the yield of monoesters of the transmitted ozon 167–200%).

EXPERIMENTAL

PMR spectra were registered on spectrometer "Tesla BS-497" with working frequency 100 MHz in CCl_4 solution at a room temperature, internal standard—HMDS.

Chromotographic analyses were conducted by the internal standard method on LHM-8MD with a katarometer, column of 200 cm length, 0.4 cm diameter, stationary phase PPMS (15%), or SE—30 (5%) on a chromaton, gas-carrier—helium, consumption—1.8 l/hr.

Cyclic acetals were produced by the procedure described in Ref. 28.

The rate of oxygen absorption was determined manometrically.[29] The concentration of the hydroperoxides was controlled iodometrically.[30] A laboratory ozonator was used for obtaining ozon.[31]

The synthesis of monoesters of glycol was carried out by the following procedures:

Oxidation with oxygen. 0.2–1 mole of acetal, calculated quantity of the catalyst, crown-ether and solvent were fed into at catalytic oxidation. Under continuous stirring and at a definite temperature dry air was bubbled at the rate of 10–15 l/hr.

Interaction of hydroperoxides and hydrogen peroxide with 1,3-dioxacylanes was carried out at 80–120°C and at the ratio of the initial reagents 1:1–1:10. Hydroperoxide and acetal were fed into a thermostating reactor or ampules, and heated for 3–5 hours. The reaction was monitored according to the changes of the hydroperoxide concentration.

Ozonation. 0.1 mole of acetal was fed into a glass reactor with a reflux condenser and ozonated at −60°C for 20–45 min., the rate of ozon–oxygen mixture feed—3 l/hr (ozon percentage—2–3%).

The isolation of the monoesters of glycol was carried out by way of vacuum distillation.

References

1. H. Mitteil, H. Seyfarth and A. Hesse, *Chem. Ber.* **100**, 2491 (1976).
2. A. Rieche, F. Schmitz and F. Beyer, *Chem. Ber.* **91**, N9, 1935–1941 (1958).
3. Y. Rebek and R. McCready, *Tetrahedron Letters* N42, 3889–3892 (1971).
4. E. M. Kuramshin, Y. B. Imashev, S. S. Zlotsky and D. L. Rakhmankulov, *Izv. vusov. Khimiya i khim. tekhnol.* N27, **1**, S. 13–30 (1984).
5. V. K. Gumerova, Sinetz nekotorykh reaktsy i svoistva lineynykh i tsyklitcheskikh atsetaley.—Avtoref. diss. kand. khim. nauk. Ufa, 124 s (1984).
6. M. A. Molavko, Prevrascheniya tsiklischeskikh acetaley pod deystviyem organicheskikh gidroperoksidov. Avtoref. diss. kand. khim. nauk. Ufa, 124 s (1986).
7. H. M. Emanuel, E. T. Denisov and Z. K. Maizus, Tsepnye reactsii okisleniya uglevodorodov v zhidkoy faze. *M*: *Nauka,* 375 s (1985).
8. E. T. Denisov, N. I. Mitskevitch and B. E. Agabekov, Mekhanizm zhidkofaznogo okisleniya kislorodovodorodnykh soedineniy. *Minsk; Nauka itekhnika,* 334 s (1975).
9. E. M. Kuramshin, V. K. Gumerova, L. G. Kulak, S. S. Zlotsky and D. L. Rakhmankulov, *Zhur. Org. khimii.* T. 55, N7, S. 1611–1615 (1985).
10. G. F. Pustarnakova and V. F. Solanikov, *Neftekhimiya* N1. S. 124–129 (1975).
11. E. M. Kuramshin, S. S. Zlotsky, V. A. Dyachenko and D. L. Rakhmankulov, *Neftekhimiya* T. 22, N1, S. 72–75 (1982).
12. E. M. Kuramshin, V. A. Dyachenko, S. S. Zlotsky and D. L. Rakhmankulov, *Neftekhimiya* T. 22, N5, S. 620–622 (1982).
13. E. M. Kuramshin, V. A. Dyachenko, S. S. Zlotsky and D. L. Rakhmankulov, *Neftekhimiya* T. 22, N5, S. 620–622 (1982).
14. E. M. Kuramshin, V. K. Gumerova, Y. M. Shaulsky, S. S. Zlotsky and D. L. Rakhmankulov, *Plastmassy* N6, S. 6–8 (1983).
15. E. M. Kuramshin, V. A. Dyachenko, U. M. Shaulsky, S. S. Zlotsky and D. L. Rakhmankulov, *Dokl. AN SSSR* N1, S. 118–120 (1984).
16. E. M. Kuramshin, S. S. Zlotsky, V. A. Dyachenko and D. L. Rakhmankulov, IV Mezhdunarodny simposium po gomogennomu katalizu. *Tez. Dokl. Leningrad* T. 2, S. 204 (1984).
17. E. M. Kuramshin, M. V. Kochinashvili, S. S. Zlotsky and D. L. Rakhmankulov, *DAN SSSR* T. 279, N6, S. 1392–1394 (1984).
18. P. Deslongchamps, *Tetrahedron* V. 31, N20, P. 2463–2490 (1975).
19. F. Kovac and V. Plesnicar, *J. Chem. Soc., Chem. Commun.* N3, P. 122–124 (1978).
20. F. Kovac and V. Plesnicar, *J. Amer. Chem. Soc.* V. 101, P. 2677 (1979).
21. D. L. Rakhmankulov, E. M. Kuramshin and S. S. Zlotsky, *Uspechi khimii,* T. 54, N6, S. 923–940 (1985).
22. E. M. Kuramshin, L. G. Kulak, S. S. Zlotsky and D. L. Rakhmankulov, Tez. Dokl. I Mezhdunorodnogo simposiuma. Ozonnaya destruktsiya polymerov. Sofiya, Bolgariya, S. 28 (1984).
23. E. M. Kuramshin, L. G. Kulak, S. S. Zlotsky and D. L. Rakhmankulov, *Izvestiya po khimii. BAH* T. 18, S. 236–239 (1985).
24. E. M. Kuramshin, M. A. Molavko, S. S. Zlotsky and D. L. Rakhmankulov, *Izvestiya vuzov: khimiya i khim. technologiya.* T. 28, W. 9. S. 23–25 (1985).
25. E. M. Kuramshin, M. A. Molavko, S. S. Zlotsky and D. L. Rakhmankulov, *ZhOKh.* T. 55, V. 6, S. 1393–1396 (1985).
26. E. M. Kuramshin, M. A. Molavko, S. S. Zlotsky and D. L. Rakhmankulov, *Dokl. AN SSSR* T. 285, N5, S. 1131–1133 (1985).
27. E. M. Kuramshin, V. K. Gumerova, V. A. Dyachenko and L. G. Kulak, i dr. *ZhOKh* T. 58, N5. S. 1069–1075 (1988).

28. D. L. Rakhmankulov, R. A. Karakhanov, S. S. Zlotsky, E. A. Kantor, U. B. Imashev and A. M. Syrkin, Khimiya i technologiya 1,3-dioksacyclanov. Tekhnologiya organicheskikh veschestv. Itogi nauki i tekhniki. *M: VINITI* t. 5, 288 s (1975).
29. N. M. Emanuel, G. E. Zaikov and Z. K. Mairus, Tsepnye reaktsii okisleniya uglevodorodov v zhidkoy faze. *M.: Nauka* 375 s (1967).
30. B. L. Antonovsky, M. M. Buzlanova, Analyticheskaya khimiya organicheskikh peroksidnykh soedineniy. *M; Khimiya* 308 s (1978).
31. V. P. Vendillo, Y. M. Emelyanov and Y. B. Filipov, *Zavodskaya laboratoriya* T. 25, V. 11, S. 1401-1402 (1959).