

LIQUID-PHASE RADICAL REACTIONS OF ACETALS AND
THEIR ANALOGUES AT HIGH PRESSURE

by

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Results, concerning the influence of high pressure on the rates and directions of homolytic transformations of cyclic, linear-cyclic and linear acetals and their N- and S-containing heteroanalogues are summarized and analyzed.

High pressure is widely used to obtain information on the mechanism of chemical reactions, the structures of the transition states, and the effects of various factors on the rates and directions, i.e. it is used for purposes of chemical synthesis [1-4]. Just as data can be obtained on the energy parameters in the knowledge of the displacement of equilibrium and the variations in the process rates with changes in temperature, the volume characteristics of reactions behave as thermodynamic variables with the variation of pressure.

It has been established on the basis of transition state theory that the rate of reaction depends on pressure (p) (Eq. (1)), where ΔV^\ddagger is the volumetric activation effect, numerically equal to the

$$\left(\frac{\partial \ln k}{\partial p} \right)_T = \frac{\Delta V^\ddagger}{RT} \quad (1)$$

change in volume on the formation of one mole of the activ-

ated complex from the interacting particles.

An analogous equation is known from chemical thermodynamics. It characterizes the dependence of the equilibrium constant on pressure, but instead of ΔV^\ddagger it contains ΔV , the volumetric change during the reaction. Equation (1) shows that k decreases with the increase of pressure, if $\Delta V^\ddagger > 0$, i.e. if, during the formation of the transition state from the initial particles, a volume increase occurs. For example, it may be presumed that in the homolytic decay of tert-butyl peroxide the breaking bond O-O is lengthened in the transition state and the volume of the latter will be larger than that of the initial molecule. Indeed, the known data show that the decay rate of tert-butyl peroxide decreases with the increase of pressure.

The majority of chemical reactions are accelerated by the increase of pressure ($\Delta V^\ddagger < 0$) as they are bimolecular. In the formation of the transition state in a bimolecular reaction, the initial particles come so close together that the distance between them is less than the sum of their van der Waals radii. As a result, the volume of the transition state is less than the sum of the volumes of the initial particles. Radical addition reactions to a double bond (the growth of the chain during polymerization), for instance, and the extraction of H and Cl atoms by a radical (radical substitution) accelerate with pressure increase.

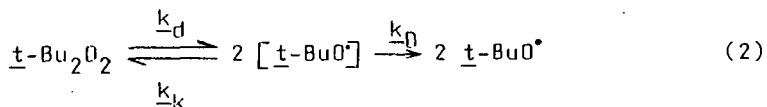
Among free radical reactions there are fast processes (such as recombination and disproportionation), including the termination step in radical-chain processes, the rate of which is determined by diffusion factors and therefore depends on the viscosity of the medium. Since the viscosity increases considerably with the increase of pressure, the rates of such reactions decrease, though they remain bimolecular. On the other hand, it is not difficult to imagine that monomolecular radical reactions might also be accelerated by pressure, e.g. the formation of cyclic radicals from linear radicals by intramolecular addition of a free radical centre to an unsaturated bond. This may be expected because the density of cyclic combinations is usually higher

than that of the linear combinations containing the same number of atoms in the chain.

The value of ΔV^\ddagger is determined experimentally by measuring the rates of reaction at different pressures. The logarithm of the rate constant is then plotted against pressure. ΔV^\ddagger is calculated by analytical or graphical differentiation of this function in accordance with Eq. (1) at the point of atmospheric pressure. As the function is usually non-linear, the differentiation method requires a large number of exact experimental data, and even then some uncertainties remain. In this respect, a number of methods for the calculation of ΔV^\ddagger have been suggested. Among them, a very simple method deserves attention. This was proposed by Gonikberg and El'yanov [1, 5] and is based on the linear correlation of free energies with the change of pressure. This method allows the determination of ΔV^\ddagger from a limited number of data, through the linear dependence of $\log k$ on Φ , characterizing the pressure. This method is used in the present work.

The kinetically determined rate of reaction is usually a complex constant, including several rate constants of more or less simple reactions, connected with each other in different ways depending on the process mechanism. In such cases the volumetric activation effect ΔV^\ddagger is obtained from the function $\log k$ vs. p . The essence of the volumetric activation effect can be seen in the following example.

tert-Butyl peroxide ($t\text{-Bu}_2\text{O}_2$) decay may be represented schematically as in Eq. (2), where the



square brackets designate a cage of solvent molecules. Radicals in the cell may either diffuse from the cell with rate constant k_p , or recombine inside the cell (k_k) with formation of the initial peroxide (k_d is the rate of radical formation in the cell).

The rate of decay w_p may be presented as in Eq (3), where f is the fraction of radicals leaving

$$\underline{w}_p = 2 f k_d [C] \quad (3)$$

the cell, connected with the rate constants k_k and k_D by the dependence $\frac{1-f}{f} = \frac{k_k}{k_D}$, and $[C]$ is the concentration of peroxide. Therefore, $\frac{k_D}{k_p} = 2f k_d$. Taking logarithms, with subsequent differentiation with respect to p and multiplication by \underline{RI} gives Eqs. (4) and (5).

$$\Delta \underline{V}_p^\ddagger = \Delta \underline{V}_d^\ddagger + \Delta \underline{V}_f^\ddagger \quad (4)$$

$$\Delta \underline{V}_f^\ddagger = -\underline{RI} \left(\frac{\partial \ln f}{\partial p} \right)_T \quad (5)$$

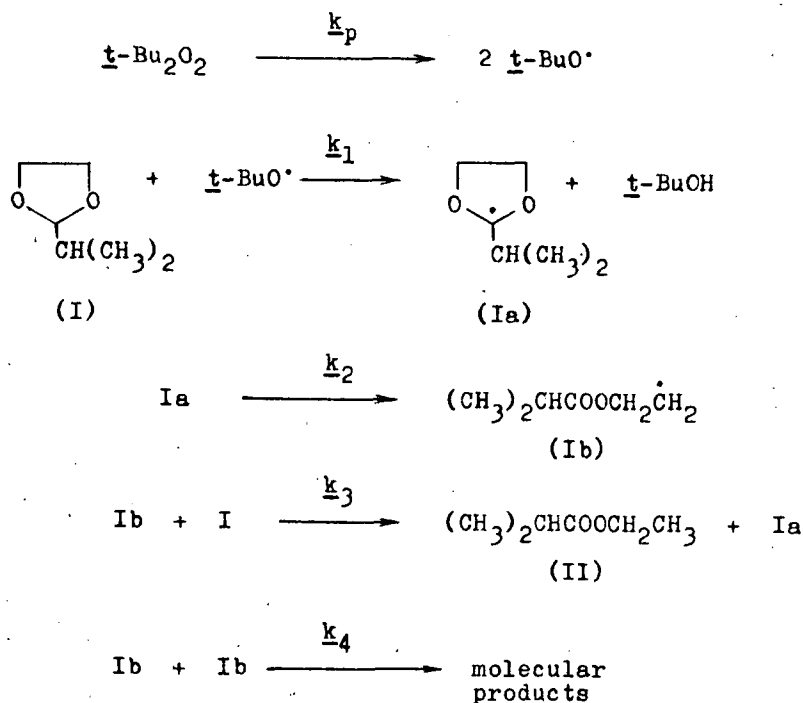
The present article considers generalized information on the influence of high pressure on the rates and directions of the homolytic transformation of acetals in solution.

It is known that linear and cyclic acetals [6-9] and their nitrogen- and sulphur-containing analogues [10-13] are transformed in the presence of radical initiators at 393-423 K into carboxylic esters, amides or thioesters, respectively.

The process has a non-ramified chain free radical mechanism with a quadratic termination on rearranged (eliminated in the case of linear acetals) radicals [6,7, 10].

The limiting stage of isomerization (fragmentation) is the reaction of hydrogen atom abstraction from the substrate by a rearranged radical [6, 7, 10]. These reactions are characterized by very short chain length, and therefore by a high specific expenditure of initiator. Attempts have been made by some authors to intensify these reactions through the application of high pressure and to study its influence on the kinetics and mechanisms of these reactions.

Thus, in the homolytic liquid-phase isomerization of 2-isopropyl-1,3-dioxolane (I) into ethyl isobutyrate (II) (Scheme I), initiated by $t\text{-Bu}_2\text{O}_2$ at 403 K and pressure up to 10000 kg/cm² [14, 15] the decay rate constant of $t\text{-Bu}_2\text{O}_2$, k_p , decreases. The length of the kinetic chain (ν), defined as the ratio of the initial rate of ethyl isobutyrate formation (\underline{w}_{II}) to the rate of initiation (\underline{w}_i), numerically equal to the accumulation rate of tert-butyl



Scheme I

alcohol ($w_i = w_{\text{t-BuOH}}$), increases a little with the increase of pressure.

A considerable decrease of the initiation rate, which is not compensated by a small increase of the kinetic chain length at the same time, is the cause of the formation rate decrease of ester II at increasing pressure. The kinetic parameter $k_3/\sqrt{k_4}$, characterizing the reactivity of 2-isopropyl-1,3-dioxolane (I) in free radical isomerization, practically does not change with the change of pressure (Table I), which means that $\Delta V_3^+ - \frac{1}{2} \Delta V_4^+ \approx 0$.

In the discussed process, the chain is propagated by carbon-centred radicals; in the abstraction of hydrogens, ΔV^+ is negative but has a comparatively small value: $\Delta V_3^+ \approx -4 \text{ cm}^3/\text{mol}$ [14, 15, 18]. At $\Delta V_3^+ - \frac{1}{2} \Delta V_4^+ \approx 0$; $\Delta V_4^+ \approx 8 \text{ cm}^3/\text{mol}$, i.e. the termination is accelerated by pressure and proceeds

not in the diffusion but in the kinetic sphere [3]. The conclusion of the acceleration of the termination with pressure increase is true only when the cyclic radical does not play a perceptible part in the termination.

Thus, the increase of pressure does not lead in this case to acceleration of the process, but decreases the expenditure of the initiator approximately 3-fold, at the expense of the increase in length or the kinetic chain from 5 to 14 (Table I).

Isomerization of non-symmetric cyclic acetals leads to the formation of two isomeric esters [16]. Thus, the reaction of 4-methyl-1,3-dioxane (III) initiated by $t\text{-Bu}_2\text{O}_2$ at 403 K yields *n*-butyl formate (IV) and *sec*-butyl formate (V) in a ratio of 6:1 at normal pressure [16] (Scheme II). In refs. [15, 17], the influence of high pressure on the products of this reaction was studied; for this purpose the kinetics of accumulation of esters IV and V at various pressures was investigated.

With the increase of pressure, as with 2-isopropyl-1,3-dioxolane, the initiation rate in the system decreases similarly to the rate constant of $t\text{-Bu}_2\text{O}_2$ decay (k_p) [15, 17] (Table II). With the increase of pressure, the selectivity of formation of *n*-butyl formate (IV) increases. This can be explained in that in the process of monomolecular rearrangement of the 4-methyl-1,3-dioxo-2-cyclohexyl radical (IIIa) in the transition state the C(4)-O(3) bond is lengthened to a smaller extent than the C(6)-O(1) bond, the result being that the volume increase is greater in activation in the latter case. The difference in the volumetric activation effects of the C(6)-O(1) and C(4)-O(3) bonds is $3.0 \text{ cm}^3/\text{mol}$.

Parameter $k_3/\sqrt{k_4}$, characterizing the reactivity of 4-methyl-1,3-dioxane (III) in the free radical isomerization, increases a little, while the kinetic chain length \bar{v} increases more with pressure (up to 7500 kg/cm^2) than in the case of 2-isopropyl-1,3-dioxolane (I). This is possibly connected with the fact that in 4-methyl-1,3-dioxane isomerization secondary formyloxybutyl radicals (IVa) take part in the chain lengthening and the reaction accelerates more

Table I

Liquid-phase radical isomerization of 2-isopropyl-1,3-dioxolane (I) to ethyl isobutyrate (II) under high pressure [14, 15]

$T = 403 \text{ K}$, $\tau = 2 \text{ hr}$, $[t\text{-Bu}_2\text{O}_2] = 0.4 \text{ mol/l}$, $[I] = 7.6 \text{ mol/l}$

Pressure (kg/cm ²)	[II] (mol/l)	[t-BuOH] (mol/l)	$w_{II} \cdot 10^5$ (mol/l.s)	$w_{t\text{-BuOH}} \cdot 10^5$ (mol/l.s)	ν	$k_p \cdot 10^5$ (s ⁻¹)	$\frac{k_3^a}{\sqrt{k_4}} \cdot 10^3$
1	0.55	0.11	7.6	1.5	5.0	1.9	3.6
2000	0.56	0.06	7.8	0.9	9.0	1.1	4.9
5000	0.38	0.03	5.3	0.4	12.2	0.5	4.7
10000	0.22	0.02	3.1	0.2	14.2	0.27	3.9

$$\frac{k_3^a}{\sqrt{k_4}} = \frac{w_{II}}{[I] \sqrt{w_{t\text{-BuOH}}/2}}$$

Table II

Dependence of formation rate of n-butyl formate (IV) and sec-butyl formate (V) and constants k_p and $k_3/\sqrt{k_4}$ on pressure in 4-methyl-1,3-dioxane (III) isomerization [15]. $T = 403$ K, $[t\text{-Bu}_2\text{O}_2] = 0.5$ mol/l, $[\text{III}] = 7.0$ mol/l

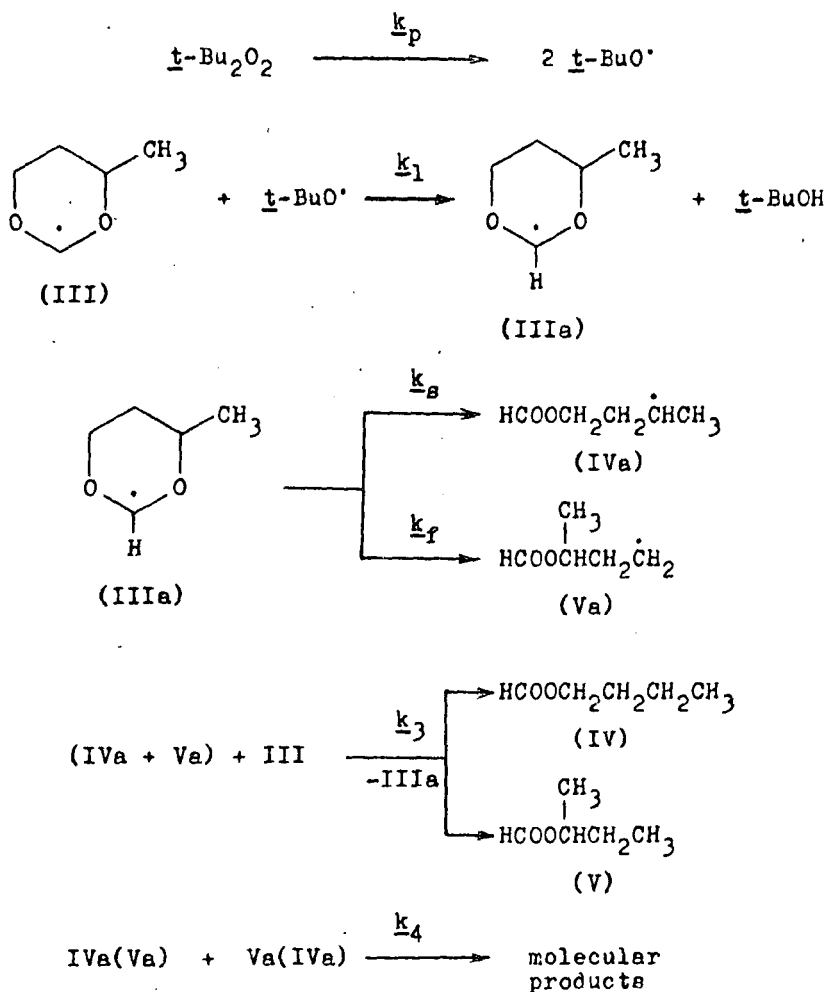
Pressure (kg/cm ²)	$w_{t\text{-BuOH}}$ (mol/l.s)	$k_p \cdot 10^6$ (s ⁻¹)	$w_{IV} \cdot 10^5$ (mol/l.s)	$w_V \cdot 10^5$ (mol/l.s)	$\frac{w_{IV}}{w_V}$	w_{IV+V}^a (mol/l.s)	v^b	$\frac{k_3}{\sqrt{k_4}} \cdot 10^3$ (l/mol.s) ^{1/2}
1	2.7	27.0	1.85	0.31	5.9	2.2	0.8	0.9
2500	1.6	16.0	2.40	0.33	7.2	2.7	1.7	1.4
5000	1.2	12.0	2.55	0.32	8.0	2.9	2.4	1.6
7500	0.6	5.8	2.1	0.25	8.6	2.4	3.9	2.2
10000	0.3	2.9	0.05	0.08	10.0	0.9	3.1	1.1

$$^a w_{IV+V} = w_{IV} + w_V$$

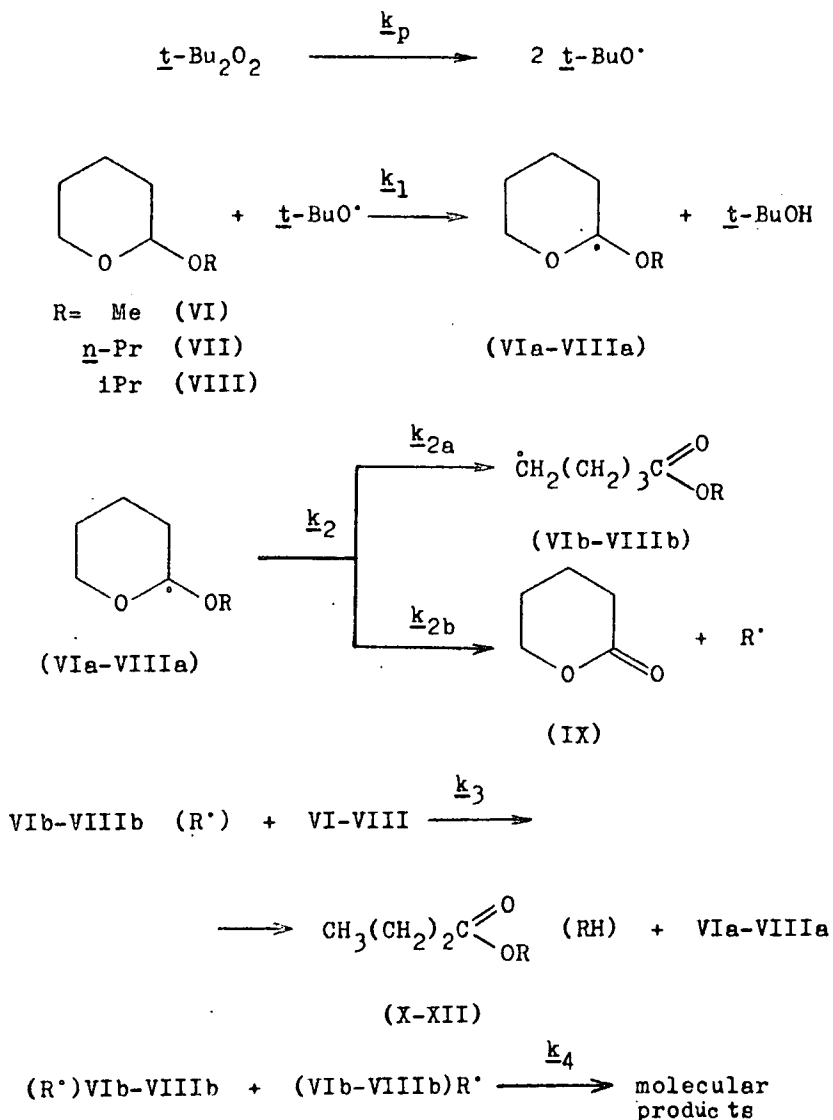
$$^b v = \frac{w_{IV+V}}{w_{t\text{-BuOH}}}$$

quickly in their presence [18].

It has already been shown [19, 20] that the homolytic transformation of linear-cyclic acetals of 2-alkoxytetrahydropyrans (VI-VIII), initiated by $t\text{-Bu}_2\text{O}_2$ at 403 K, leads to the formation of two products: δ -valerolactone (IX) and the corresponding alkyl ester of valeric acid (X-XII) (Scheme III). As a result of experiments with compounds



Scheme II



Scheme III




VI-VIII at different pressures, it has been established that the reaction products do not change qualitatively, but the correlation of the isomerization products (k_{2a}) and fragmentation products (k_{2b}) depends essentially on pressure [21, 22].

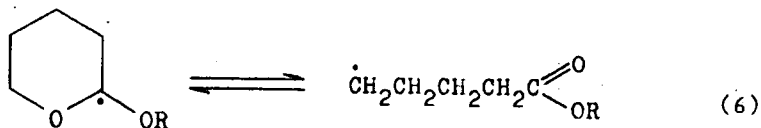
With pressure increase, the ratio of lactone to ester is increased (Table III). Thus, at atmospheric pressure 2-methoxytetrahydropyran (VI) is transformed almost entirely into the isomeric ester methyl valerate (X), while at 10000 kg/cm^2 the yield of δ -valerolactone (IX) is close to that of ester X. The observed change in the lactone:ester ratio (scores of times for VI) in response to pressure is impossible to explain [21, 22] by the difference in chain lengthening alone on the formation of the transition state. From the difference in volumetric activation effect of the two reactions (lactone formation and ester formation from VI) the quantity of $25 \text{ cm}^3/\text{mol}$ is obtained, which is incompatible with any chain lengthening in the cycle. The most probable explanation of the observed effect is an equilibrium (Eq. (6)). With the increase of pressure, this equilibrium is shifted to the left for the formation of a compound with higher density, the volumetric effect of this reaction being nearly $15 \text{ cm}^3/\text{mol}$. This suggestion provides at least a qualitative explanation of the results obtained. In the presence of the equilibrium, the lactone:ester ratio is connected with a large number of kinetic parameters and numerical interpretation of the results is in general very difficult problem. The above feature allows an explanation of the comparatively small change in the lactone:ester ratio (less than 3-fold at 10000 kg/cm^2) for VIII. It is quite possible that in this case cyclization does not take place, for example, because of spatial difficulties and because of the presence of the bulkier isopropyl group, the lactone:ester ratio being determined by the fission rate ratio of the corresponding bonds. In such cases the change in the lactone:ester ratio under pressure will be determined by the difference in the transition state volumes, originating from the lengthening of the endo- and exocyclic bonds. According to Table III this difference averages $6 \text{ cm}^3/\text{mol}$,

Table III

Homolytic transformations of 2-alkoxytetrahydropyrane at high pressure [21, 22]

 $T = 403 \text{ K}$, $[t\text{-Bu}_2\text{O}_2] = 0.3 \text{ mol/l}$, $\tau = 2 \text{ hr}$

Compound (mol/l)	Pressure (kg/cm ²)	[lactone].10 (mol/l)	[ester].10 (mol/l)	$\frac{[\text{lactone}]}{[\text{ester}]}$	[t-BuOH].10 (mol/l)	ν_{ester}	ν_{Σ}
 VI (8.26)	1	0.05	3.50	0.01	1.20	2.9	2.96(3.0)
	2500	0.15	2.00	0.07	0.45	4.4	4.77(4.8)
	5000	0.35	1.50	0.23	0.20	7.5	9.2
	7500	0.45	0.90	0.50	0.10	9.0	13.5
10000	0.50	0.70	0.70	0.10	7.0	12.0	
 VII (6.42)	1	0.29	1.43	0.20	0.78	1.8	2.2
	2500	0.25	0.75	0.33	0.28	2.7	3.6
	5000	0.23	0.30	0.77	0.20	1.5	2.6
	10000	0.18	0.10	1.80	0.12	0.8	2.3
 VIII (6.47)	1	0.80	0.25	3.20	0.77	0.3	1.4
	2500	0.70	0.20	3.50	0.28	0.7	3.2
	5000	0.55	0.10	5.50	0.16	0.6	4.1
	10000	0.45	0.05	9.00	0.08	0.6	6.2



which seems quite admissible.

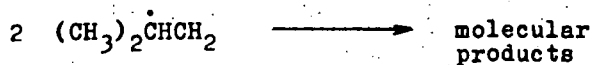
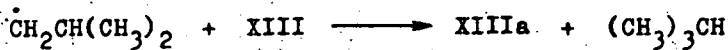
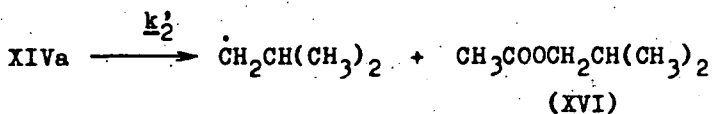
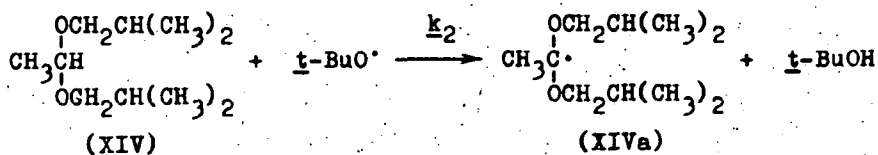
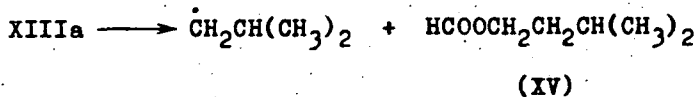
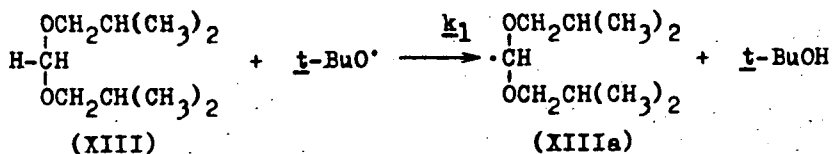
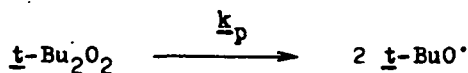
Homolytic transformations of linear acetals under high pressure has been investigated on the examples of diisobutoxymethane (XIII) and 1,1-diisobutoxyethane (XIV), which were converted into isobutyl formate (XV) and isobutyl acetate (XVI) in reactions initiated by $t\text{-Bu}_2\text{O}_2$ at 403 K [23, 24].

The transformations of acetals XIII and XIV under the influence of $t\text{-Bu}_2\text{O}_2$ (in accordance with [7-9]) are described by Scheme IV in which the termination is the result of recombination in the presence of radicals $\text{CH}_2\text{CH}(\text{CH}_3)_2$.

The simultaneous formation of esters XV and XVI is a result of a chain process in which two substrates are involved. The formation rate ratio of the esters, $\frac{w_{\text{XV}}}{w_{\text{XVI}}}$, is determined by the difference in the reactivities of acetals XIII and XIV, i.e. by the tendencies of the corresponding C(1)-H bonds, adjacent to the two oxygen atoms, to undergo homolytic breaking [23, 24]. With the increase of pressure the initiation rate in the system decreases, which in turn causes a decrease in the rates of formation of esters XV and XVI (Table IV).

The difference in the activities of acetals XIII and XIV increases under pressure (Table IV), as demonstrated by the ratio of the formation rates of isobutyl acetate and isobutyl formate, $\frac{w_{\text{XVI}}}{w_{\text{XV}}}$, i.e. under pressure the homolytic breaking of the tertiary bond C(1)-H in 1,1-diisobutoxyethane increases to a greater degree under the influence of the radical $\text{CH}_2\text{CH}(\text{CH}_3)_2$ [23, 24]. A similar regularity has been found for substitution reactions in the presence of oxygen-centred radicals [25].

During the thermal decay of $t\text{-Bu}_2\text{O}_2$ at 403 K in a medium of N -propyl-1,3-oxazolidine (XVII) or N -propyl-2-ethyloxazolidine (XVIII), N -ethyl- N -propylformamide (XIX)



Scheme IV

Table IV

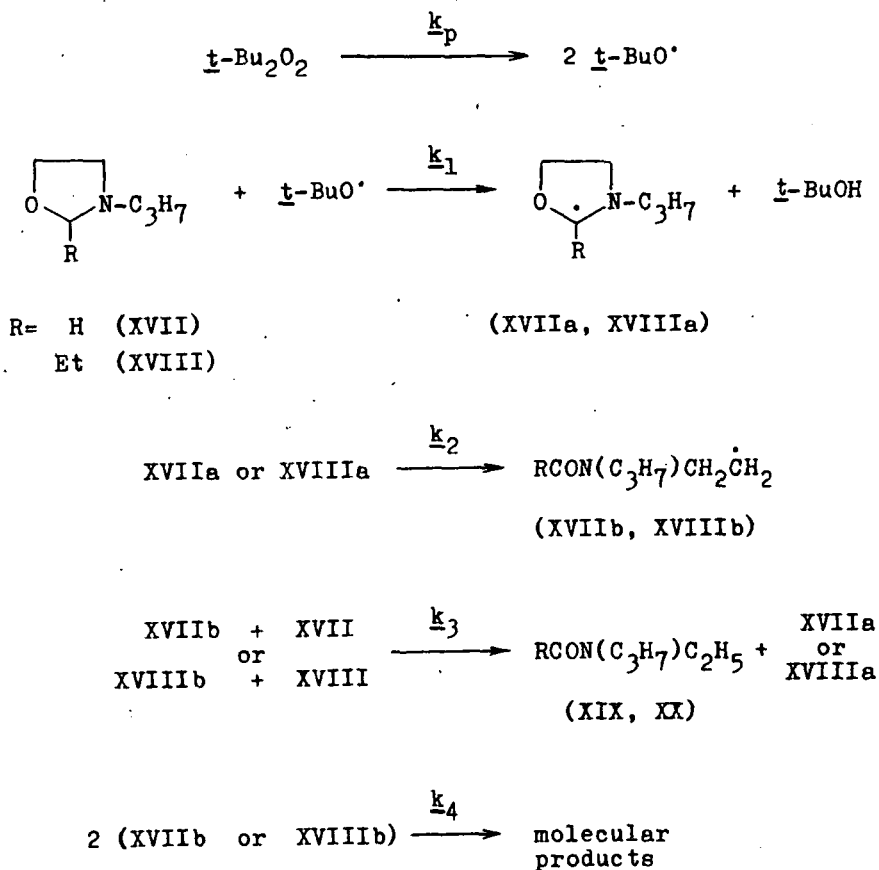
Homolytic transformations of 1,1-diisobutoxyalkanes (XIII, XIV) in the liquid phase at high pressure [23, 24]

$T = 403 \text{ K}$, $[t\text{-Bu}_2\text{O}_2] = 0.4 \text{ mol/l}$, $[\text{XIII}] = [\text{XIV}] = 2 \text{ mol/l}$

Pressure (kg/cm ²)	$\frac{w_{t\text{-BuOH}}}{\text{mol/l.s}} \cdot 10^6$	$k_p \cdot 10^6$ (s ⁻¹)	$\frac{w_{\text{XV}}}{\text{mol/l.s}} \cdot 10^6$	$\frac{w_{\text{XVI}}}{\text{mol/l.s}} \cdot 10^6$	$\frac{w_{\text{XVI}}^a}{w_{\text{XV}}}$	ν
100 - 200	50.0	62.5	63.0	44.0	1.4	2.1
2500	37.3	46.5	37.5	23.0	1.7	1.6
5000	24.0	30.0	35.5	18.1	2.0	2.2
7500	13.9	17.4	32.0	13.8	2.4	3.8
10000	9.6	12.0	21.8	7.0	3.1	3.0

$$\frac{w_{\text{XVI}}^a}{w_{\text{XV}}} = \frac{k_3'}{k_3}$$

or *N*-ethyl-*N*-propylpropionamide (XX) is formed [26, 27]. At high pressure (1-10000 kg/cm²), the composition of the products does not change qualitatively [26, 27]. The formation of amides XIX and XX follows Scheme V [10]. With the increase of pressure from 1 up to 10000 kg/cm², both the initiation rate ($\underline{w}_i = \underline{w}_{t\text{-BuOH}}$) and the decay rate constant of $t\text{-Bu}_2\text{O}_2$ decrease by one order (Table V). The formation rates

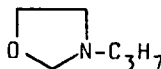
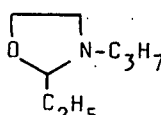


Scheme V

Table V

Kinetic parameters of homolytic liquid-phase isomerization of 1,3-oxazolidines (XVII, XVIII) under high pressure [26, 27]

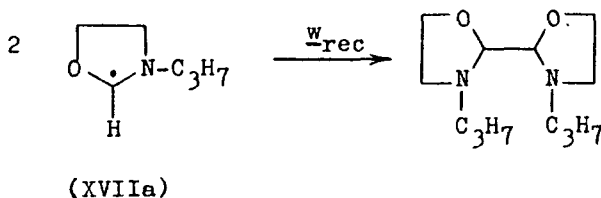
$T = 403 \text{ K}$, $[t\text{-Bu}_2\text{O}_2] = 0.4 \text{ mol/l}$ $\tau = 2 \text{ hr}$, solvent = chlorobenzene

1,3-oxazolidines	Pressure (kg/cm ²)	[t-BuOH] (mol/l)	$\frac{w_{t\text{-BuOH}}}{10^5}$	$\frac{k_p}{s^{-1}} \cdot 10^5$	[amide] (mol/l)	$\frac{w_{\text{amide}}}{10^5}$	v^a
	1	0.25	3.5	4.3	0.32	4.4	1.3
	2500	0.12	1.7	2.1	0.03	0.3	0.2
	5000	0.09	1.3	1.6	0.02	0.3	0.2
	7500	0.07	1.0	1.2	0.01	0.1	0.1
	10000	0.04	0.5	0.5	-	-	-
	1	0.25	3.5	4.4	0.38	5.4	1.5
	2500	0.10	1.4	1.8	0.06	0.9	0.6
	5000	0.08	1.1	1.4	0.01	0.2	0.1
	7500	0.06	0.9	1.2	0.01	-	-
	10000	0.03	0.3	0.4	-	-	-

$$a \quad v = \frac{w_{\text{amide}}}{w_{t\text{-BuOH}}}$$

of amides XIX and XX at the same pressure decrease together with the length of the kinetic chain, in contrast with the transformations of cyclic [14], linear-cyclic [21] and linear [23] acetals.

Consideration of all the data testifies to the fact that, in the oxazolidine reactions, chain opening takes place in the cyclic radicals too. This has been confirmed in work [28] in which the ratio of the rates of formation and recombination of cyclic radicals XVIIa (w_{rec}) and of initiation (w_i) at 1 and 7500 kg/cm² was determined (Scheme VI).



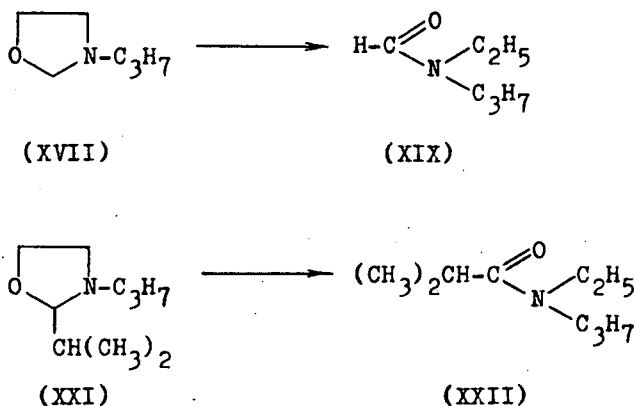
Scheme VI

At a pressure of 1 kg/cm² the ratio $2 w_{rec}/w_i = 0.1$, i.e., only 10% of the cyclic radicals formed take part in recombination while at a pressure of 7500 kg/cm² the ratio $2w_{rec}/w_i = 0.4$, i.e. the number of cyclic radicals XVIIa taking part in the recombination increases 4-fold. Thus, with the increase of pressure rate of monomolecular rearrangement of 1,3-oxaza-2-cyclopentyl radical into linear radical XVIIb decreases sharply, while the proportion of cyclic radicals XVIIa taking part in chain opening increases.

The most probable explanation is that pressure accelerates the recombination of cyclic radicals (termination) and slows down the rate of their rearrangement into linear radicals. Further, the latter effect is possibly essential as is the case with the existence of the cyclic radical \rightleftharpoons linear radical equilibrium in the tetrahydropyran reactions (Eq. (6)). This increase in the number of radicals taking part in the termination corresponds to a

volumetric activation effect of $14 \text{ cm}^3/\text{mol}$, which is difficult to explain by the difference in chain lengthening alone.

Thus, in [26, 27] the influence of high pressure on the relative activity of 1,3-oxazolidines (XVII, XXI) (Scheme VII) in radical isomerization was studied via the



Scheme VII

competing reactions method and it was established that with the increase of pressure up to 2500 g/cm^2 the relative yield of the N-ethyl-N-propylisobutyramide (XXII), which is isomeric to 2-isopropyl-N-propyl-1,3-oxazolidine (XXI), increases in comparison with that of the formamide XIX formed from N-propyl-1,3-oxazolidine (XVII) (Table VI). This increase conforms to a volumetric activation effect of $14 \text{ cm}^3/\text{mol}$, the difference in chain lengthening hardly being the reason for this.

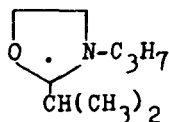
The most logical explanation seems to be that in one of the cases (compound XXI) the linear rearranged radical does not recycle, while the other case (compound XVII) is characterized by the equilibrium cyclic radical \rightleftharpoons linear radical being displaced, as noted above, to the left. Such a difference in the volumetric effects as $14 \text{ cm}^3/\text{mol}$ is then possible. Unfortunately, this is not the only "logical" explanation. As pointed out above, a recombination reaction

Table VI

Influence of high pressure on the relative activity of 1,3-oxazolidines in radical isomerization [26, 27].
 $T = 403 \text{ K}$, $[t\text{-Bu}_2\text{O}_2] = 0.5 \text{ mol/l}$, $[\text{XVII}] = [\text{XXI}] = 2 \text{ mol/l}$,
 solvent = chlorobenzene

Pressure (kg/cm^2)	[XIX] (mol/l.)	[XXII]	$\frac{[\text{XXII}]}{[\text{XIX}]}$
1	0.171	0.121	0.7
1000	0.082	0.082	1.0
2000	0.040	0.052	1.2
2500	0.035	0.051	1.4

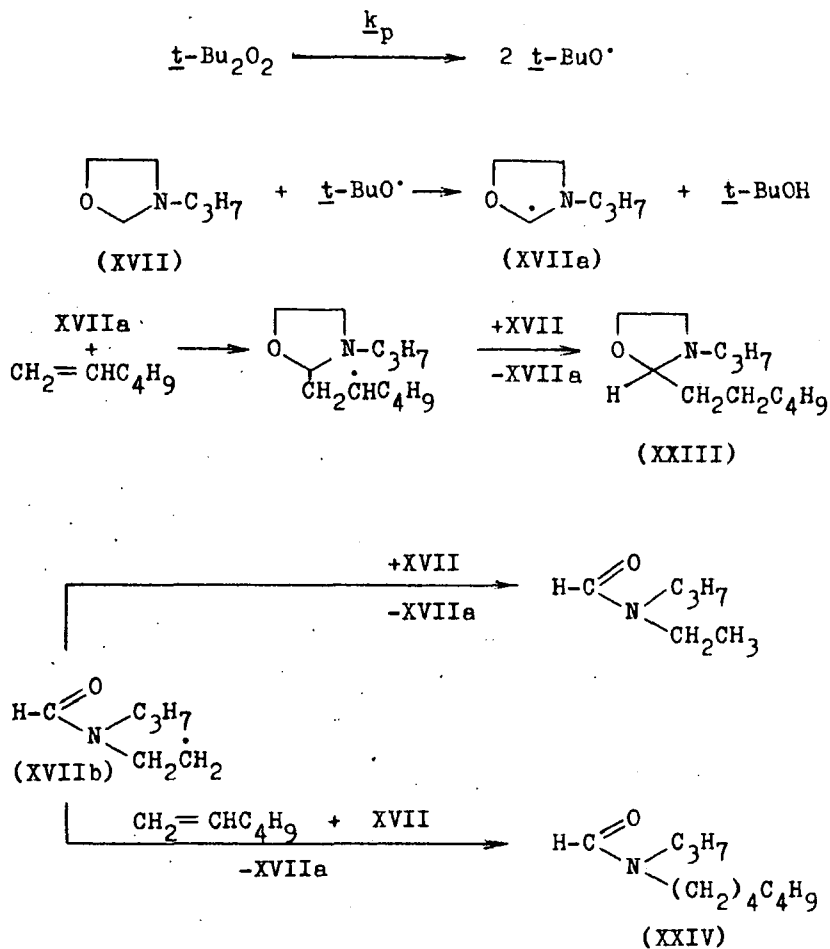
of the cyclic radical XVIIa originating from XVII has been observed, but such a reaction for XXIa is not known. If it does not exist, and recombination of the radical XVIIa accelerates with the increase of pressure then this would account for the marked increase of $[\text{XXII}]/[\text{XIX}]$.



(XXIa)

Investigations showed [27, 28] that, with the application of high pressure, it is possible to regulate the ratio of cyclic and linear products in the homolytic addition of 1,3-oxazolidines to terminal olefins. Thus, during the reaction of *N*-propyl-1,3-oxazolidine (XVII) with hexene-1 in the presence of $t\text{-Bu}_2\text{O}_2$ at 423 K, when the pressure is raised from 1 to 10000 kg/cm^2 the rate of cyclic product formation (XXIII) increases 2-fold (Scheme VIII, Table VII) [27, 28].

With the increase of pressure the decrease in rate of the monomolecular rearrangement of 1,3-oxaza-2-cyclopentyl



Scheme VIII

radical (XVIIa) means that its participation in the addition to hexene-1 increases. Simultaneously, the proportion of rearranged amidoalkyl radicals (XVIIb) participating in the formation of the linear addition product (XXIV) decreases [27, 28].

So much for a purely qualitative interpretation of the effect. However, if an attempt is made to interpret it from even a semiquantitative aspect, this explanation is open to

Table VII

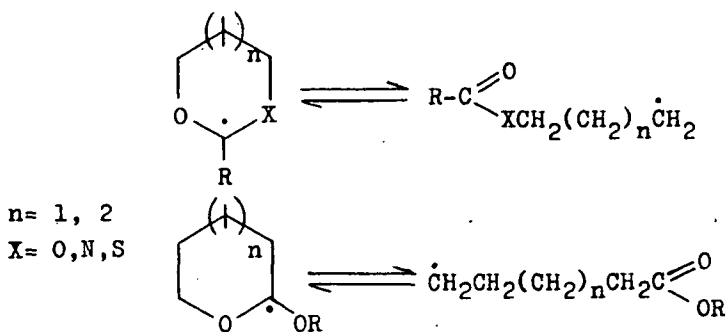
Influence of high pressure on the composition of products of radical addition of *N*-propyl-1,3-oxazolidine to hexene-1. [27, 28].

T = 423 K [hexene-1] = 0.5 mol/l, [*t*-Bu₂O₂] = 0.3 mol/l, [XVII] = 4 mol/l, solvent = chlorobenzene

Pressure (kg/cm ²)	$\frac{[XXIV]}{[XXIII]}$
1	1
1000	1.1
2500	1.2
5000	1.7
7500	1.8
10000	2.0

criticism in view of the modest nature of the effect. It seems necessary to take into account the influence of different recombination reactions on the yields of products XXIII and XXIV.

Analysis of the results permits the assumption that, in many cases of homolytic transformation of 1,3-oxaheterocycloalkanes under high pressure an equilibrium isomerization of cyclic radicals into linear acylheteroalkyl radicals takes place, with cyclization of the latter as a result of intramolecular addition to a C=O bond (Scheme IX).



Scheme IX

With the increase of pressure, the equilibrium is shifted to the left.

In general, the available data indicate that pressure fails to stimulate the homolytic transformation of acetals and their heteroanalogues, though it substantially influences the rates of the separate stages and changes the directions of the reactions noticeably.

For the decay of peroxides and nitrogen compounds $\Delta V_{\text{d}}^{\ddagger}$ is accepted as equal to 3-5 cm³/mol [3]. In accordance with data on *t*-Bu₂O₂ decay in different acetals and their heteroanalogues and Eq. (5), in all solvents studied $\Delta V_{\text{f}}^{\ddagger}$ has a positive value varying in the wide range 5-25 cm³/mol (Table VIII). Thus the radical fraction yielded by the "cell"

Table VIII

Volumetric effects of decay activation of *t*-Bu₂O₂ in different solvents at 403 K.

S o l v e n t	$\frac{V_{\text{f}}^{\ddagger}}{-p}$ (cm ³ /mol)
2-isopropyl-1,3-dioxolane	10
2-propoxytetrahydropyran	11
4-methyl-1,3-dioxane	12
2-propyl-1,3-oxazolidine	13
1,1-diisobutoxyalkanes	12
<i>N</i> -propyl-2-ethyl-1,3-oxazolidine	15
2-isopropoxytetrahydropyran	17
2-methoxytetrahydropyran	19
2-cyclohexyloxytetrahydropyran	29

decreases substantially with the increase of pressure in some solvents. Certain considerations [3] suggest that, for *t*-Bu₂O₂ decay in all the solvents studied, recombination of *t*-BuO· in the "cage" takes place. The nature of the solvent has a substantial influence on the radical fraction yielded by the "cage". This may be closely connected with the different viscosity increases of the solvents under pressure and with the influence of solvent structure on the pressure-dependence of the recombination rate.

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РАДИКАЛЬНЫЕ ПРЕВРАЩЕНИЯ АЦЕТАЛЕЙ И ИХ АНАЛОГОВ В
ЖИДКОЙ ФАЗЕ ПРОИСХОДЯЩИХ ПОД ВЫСОКИМ ДАВЛЕНИЕМ

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Сопоставлены и проанализированы результаты жидкофазных гомолитических превращений циклических, линейно-циклических и линейных ацеталей и их N- и S-аналогов, происходящих под высоким давлением.