

KINETICS AND MECHANISM OF DI-*tert*-BUTYL PEROXIDE-INITIATED LIQUID-PHASE TRANSFORMATIONS OF 2-ALKOXYTETRAHYDROPYRANS

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UDC 541.124.127:547.811

The di-*tert*-butyl peroxide-initiated (by thermal decomposition) liquid-phase transformations of 2-alkoxytetrahydropyrans to the corresponding esters of *n*-valeric acid and  $\delta$ -valerolactone were studied by kinetic methods. Their ratio is determined by the structure of the alkoxy group. The reaction proceeds via a mechanism involving an unbranched chain reaction with quadratic breaking of the chains in the rearranged radicals.

It has previously been shown that homolytic rearrangement to isomeric esters is a general reaction of 2-monosubstituted 1,3-dioxacyclanes [1-3]. The parallel formation of the corresponding esters of *n*-valeric acid and  $\delta$ -valerolactone was noted in the case of mixed linear-cyclic acetals - 2-alkoxytetrahydropyrans [4, 5].

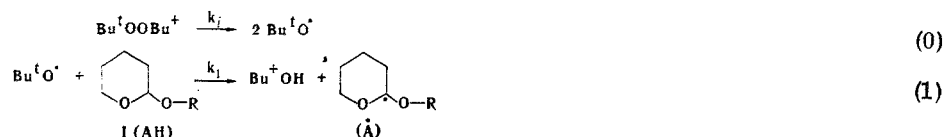
In the present research the di-*tert*-butyl peroxide-initiated liquid-phase transformations of 2-alkoxytetrahydropyrans (Ia-d) were studied by kinetic methods in order to determine the effect of the structure of the alkoxy group on the direction and rate of the reaction. In the case of cyclic acetals the *tert*-butoxyl radicals formed in the thermal decomposition of di-*tert*-butyl peroxide are consumed practically completely, as previously demonstrated [3], in the bimolecular detachment of hydrogen, and the experimentally determined initial rate of accumulation of *tert*-butyl alcohol ( $W_{alc}$ ) determines the rate of decomposition of the initiator ( $W_0$ ):

$$W_0 = \frac{1}{2} W_{alc}$$

Methyl valerate (IIa) is present in the products of conversion of Ia, but  $\delta$ -valerolactone (III), the only final product in the case of substrate Id, which contains a *tert*-butoxy group, is absent. It was also established that both types of substances - lactone III and *n*-valeric acid esters (IIb,c) - are formed from Ib and Ic, respectively.

The line of the dependence of the initial rate of accumulation of esters ( $W_E$ ), on the concentration of the 2-alkoxypyrans (Ia-c), which passes through the origin (Fig. 1), and the analogous dependence of  $W_E$  on the square root of  $W_0$  (Fig. 2) unambiguously indicate the radical chain mechanism of the isomerization, which is similar to the mechanism previously proposed for 1,3-dioxacyclanes [2, 6].

In general form, with allowance for the new reaction pathway leading to the lactone, the process can be described by the following scheme:



Ufim Petroleum Institute, Ufa 450062. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 4, pp. 456-459, April, 1977. Original article submitted May 25, 1976.

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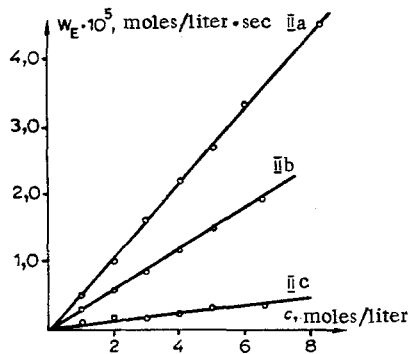


Fig. 1

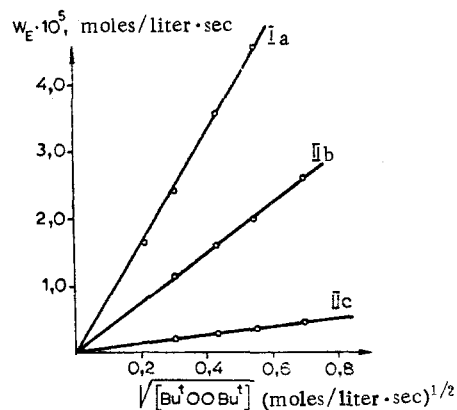


Fig. 2

Fig. 1. Dependence of the initial rate of formation of esters IIa-c ( $W_E$ ) on the substrate concentration in isooctane at 130°C; [tert-BuOOBu-tert] = 0.8 mole/liter.

Fig. 2. Dependence of the initial rate of formation of esters IIa-c ( $W_E$ ) on the square root of the initiator concentration at 130°C.

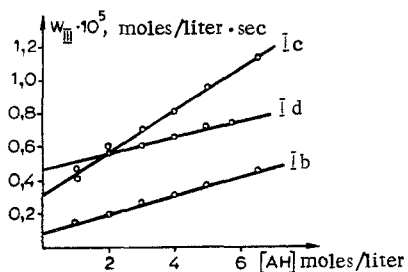


Fig. 3

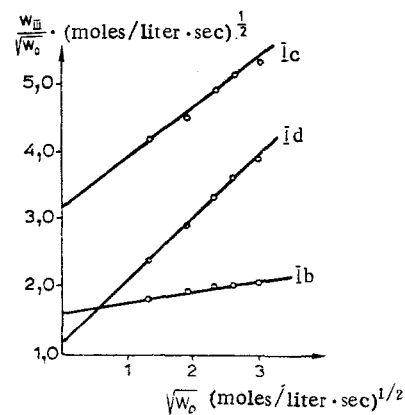
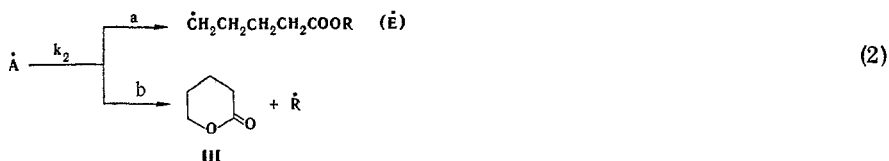


Fig. 4

Fig. 3. Dependence of the rate of accumulation of  $\delta$ -valerolactone ( $W_{III}$ ) on the substrate concentration at 130°C; [tert-BuOOBu-tert] = 0.3 mole/liter.

Fig. 4. Dependence of the ratio of the rate of accumulation of  $\delta$ -valerolactone ( $W_{III}$ ) to  $\sqrt{W_0}$  on  $\sqrt{W_0}$  at 130°C.



I, II a R = CH<sub>3</sub>; b R = n-C<sub>3</sub>H<sub>7</sub>; c R = iso-C<sub>3</sub>H<sub>7</sub>; d R = tert-C<sub>4</sub>H<sub>9</sub>

Hence, the initial rates of formation of the products are described by the following expressions:

$$W_E = \frac{k_{2a}}{k_2} \cdot \frac{k_3}{\sqrt{k_4}} \cdot [AH] \cdot \sqrt{W_0}$$

$$W_{III} = \frac{k_{2b}}{k_2} \cdot \frac{k_3}{\sqrt{k_4}} \cdot [AH] \cdot \sqrt{W_0} + \frac{k_{2b}}{k_2} \cdot W_0$$

In fact, the experimental dependences of the rate of accumulation of the lactone ( $W_{III}$ ) on the substrate concentration (Fig. 3) and of the  $W_{III}/\sqrt{W_0}$  value on the square root of  $W_0$  (Fig. 4) are in good agreement with the proposed equations.

Thus the lines that express the dependence  $W_{III} = f([AH])$  cut out segments on the axis of ordinates that are numerically equal to the  $(k_{2b}/k_2) \cdot W_0$  values, and their slopes in these coordinates correspond to the values of the expression  $\frac{k_{2b}}{k_2} \cdot \frac{k_3}{\sqrt{k_4}} \cdot \sqrt{W_0}$  (Fig. 3). At the same time, the experimental dependences  $\frac{W_{III}}{\sqrt{W_0}} = f(\sqrt{W_0})$  are expressed by lines whose slopes are close to the  $k_{2b}/k_2$  values, and the segments cut out on the axis of ordinates are numerically equal to the  $\frac{k_{2b}}{k_2} \cdot \frac{k_3}{\sqrt{k_4}}$  values (Fig. 4).

Only endocyclic cleavage of the C-O bond in the  $\dot{A}$  radical is characteristic for methoxy derivative Ia, i.e.,  $k_{2b} \ll k_{2a} \approx k_2$ , and III is not formed in appreciable amounts. The opposite extreme case is realized for 2-tert-butoxytetrahydropyran Id, in which the predominant product is cyclic ester III, i.e.,  $k_{2a} \ll k_{2b} \approx k_2$ . Compounds Ib and Ic occupy an intermediate position, since IIa, IIb, and III appear simultaneously for the corresponding  $\dot{A}$  radicals. Since the stabilities of cyclic and linear radicals of the  $\dot{A}$  and  $\dot{E}$  type are independent of the structure of substituent R, the  $k_{2a}$  values in all cases are evidently approximately identical, and the nature of the alkoxy group determines the  $k_{2b}$  value, which is higher, the higher the stability of the resulting radical R.

$$k_{2b}^{Id} \gg k_{2b}^{Ic} > k_{2b}^{Ib} \gg k_{2b}^{Ia}$$

The magnitude of kinetic parameter  $k_3/\sqrt{k_4}$  (Table 1) characterizes the reactivities of alkoxyoxacyclanes Ia-d with respect to carbon-centered radicals that continue the chain ( $\dot{E}$  or  $\dot{R}$ ). Radicals of the  $\dot{E}$  type carry on the reaction for Ia and Ib, where  $k_{2a} \gg k_{2b}$ , and the kinetic parameters of these compounds are close to one another. It is interesting to note that the  $k_3/\sqrt{k_4}$  value of  $1.8 \cdot 10^{-3}$  (liters/mole · sec)<sup>1/2</sup> is in good agreement with the analogous value for 2-methyl-1,3-dioxane [ $(k_3/\sqrt{k_4})_{Ia}^{130^\circ} = 1.84 \cdot 10^{-3}$  (liters/mole · sec)<sup>1/2</sup> [6]]. The decrease in  $k_3/\sqrt{k_4}$  on passing to Ic and particularly Id is due mainly to the decrease in the  $k_3$  value, since secondary and tertiary radicals  $\dot{R}$ , for which it is known [7] that reactions involving detachment of a hydrogen atom are energetically less favorable than for primary radicals, continue the chains. In fact, the

TABLE 1. Dependence of the Initial Rate of Accumulation of the Esters ( $W_E$ ) and  $\delta$ -Valerolactone ( $W_{III}$ ) from Tetrahydropyrans I and of Initiation ( $W_0$ ) on the Di-tert-butyl Peroxide Concentration at 130°C

Compound	Radical R in I (moles/liter)	bp, °C (mm)	$n_D^{20}$	$d_4^{20}$	tert-BuOOBu-tert	$W_0 = \frac{1}{2} W_i \cdot 10^5$ , moles/liter · sec	$W_E \cdot 10^5$ , moles/liter · sec	$W_{III} \cdot 10^5$ , moles/liter · sec	$\frac{k_{2a}}{k_2}$	$\frac{k_{2b}}{k_2}$	$k_3/\sqrt{k_4} \cdot 10^3$ , (liter/mole · sec) <sup>1/2</sup>
Ia	Methyl (8.26)	129	1.4225	0.9581	0.1	0.28	2.4	—	1	—	1.85
					0.2	0.56	3.6	—			
					0.3	0.84	4.6	—			
					0.5	1.40	5.7	—			
					0.5	1.40	5.7	—			
Ib	n-Propyl (6.40)	97/80	1.4275	0.9275	0.1	0.18	1.14	0.24	0.83	0.17	1.57
					0.2	0.36	1.59	0.36			
					0.3	0.54	1.98	0.45			
					0.5	0.90	2.57	0.63			
					0.5	0.90	2.57	0.63			
Ic	iso-Propyl (6.4 (6.47))	90/80	1.4215	0.9397	0.1	0.18	0.16	0.56	0.28	0.72	0.68
					0.2	0.36	0.24	0.87			
					0.3	0.54	0.30	1.12			
					0.5	0.90	0.38	1.58			
					0.5	0.90	0.38	1.58			
Id	tert-Butyl (5.78)	118/80	1.4260	0.9595	0.1	0.18	—	0.32	—	1	0.20
					0.2	0.36	—	0.54			
					0.3	0.54	—	0.75			
					0.5	0.90	—	1.10			
					0.5	0.90	—	1.10			

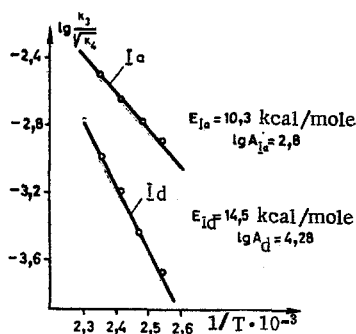


Fig. 5. Dependence of  $\log k_3/\sqrt{k_4}$  on  $1/T$  (in degrees Kelvin): [tert-BuOOBu-tert] = 0.3 moles/liter,  $E_{Ia} = 10.3$  kcal/mole,  $E_{Id} = 14.5$  kcal/mole,  $\log A_{Ia} = 2.8$ , and  $\log A_{Id} = 4.28$ .

activation energy of the isomerization of Ia in methyl valerate (IIa) is lower than for the formation of  $\delta$ -valerolactone (III) from Id (Fig. 5). However, it should be borne in mind that the above is valid under conditions where the  $k_4$  values for primary, secondary, and tertiary carbon-centered radicals of the  $\dot{E}$  and  $\dot{R}$  type are close to one another, and for this reason the comparative estimate of the reactivities of Ia-d is to a certain extent approximate.

#### EXPERIMENTAL

The starting 2-alkoxytetrahydropyrans (Table 1) were obtained by the method in [8]. Their purity was verified by gas chromatography; the absence of peroxides was monitored iodometrically, and the absence of oxo compounds was monitored from the IR spectra in the region of the characteristic absorption band of the carbonyl group. The isoctane used as the solvent was purified by the method in [9]. Freshly distilled di-tert-butyl peroxide was used.

Method Used to Conduct the Experiments. The isomerization kinetics were studied from the initial rates of formation of tert-butyl alcohol ( $W_I$ ), the ester ( $W_E$ ), and the lactone ( $W_{III}$ ) in thermostatted glass ampuls in an inert atmosphere at initiator and substrate conversion levels, respectively, of no more than 20% and 10%. The qualitative and quantitative analyses of the reaction products were analogous to those described in [1, 5]. The initiator working concentrations ranged from 0.1 to 0.6 mole/liter, and the substrate concentration ranged from 1 to 8 moles/liter. The parameters presented in Table 1 were determined with a mean square error.

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