EFFECT OF PRESSURE ON THE FREE RADICAL REACTIONS **OF 2-ALKOXYTETRAHYDROPYRANS**

V. M. Zhulin, I. Khuéidzha, E. B. Kabotvanskava, V. S. Bogdanov, and Yu. D. Koreshkov

In free radical transformations of 2-methoxy- and 2-ethoxytetrahydropyran initiated by tert-butoxy radicals at 130° C, the relative rate of formation of δ -valerolactone and valeric acid ester was found to change periodically with increase in the extent of transformation, expressed as tert-butyl alcohol (TBA) concentration. The ratio of lactone: ether concentration is determined not by the pressure (up to 1000 MPa) as suggested earlier, but by the amplitudes and phase displacement of the oscillations of the rates of formation of lactone and ester. These results are explained by changes in the physical structure of the solution in proportion to the buildup of reaction products as a result of which the reactivity of the 2-alkoxytetrahydropyranyl radical changes in respect of rupture of the endocyclic and exocyclic C-O bonds.

Keywords: pressure, 2-alkoxytetrahydropyran, free-radical reaction, synthesis of δ -valerolactone.

Preliminary results on the effect of pressures up to 1000 MPa on the ratio of the products of the transformation of 2alkoxytetrahydropyrans – δ -valerolactone and the corresponding valeric acid ester – formed on heating (130°C) solutions of di-tert-butylperoxide (DTBP) in 2-alkoxytetrahydropyrans have been reported previously [1-4].

These transformations can be represented by the following scheme:

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO \tag{1}$$

$$\bigcirc_{O} - OR + (CH_3)_3 CO \longrightarrow \bigcirc_{O} - OR + (CH_3)_3 COH$$
(1)
(1a) TBA
(2)

(3)ĊH₃CH₂CH₂CH₂COOR (1b) (4)(2)

(5) $1b + 1 \longrightarrow CH_3CH_2CH_2CH_2COOR + 1a$

$$\mathbf{R} + \mathbf{1} \longrightarrow \mathbf{R}\mathbf{H} + \mathbf{1}\mathbf{a} \tag{6}$$

Reactions (5) and (6) show that in principle the transformation of alkoxytetrahydropyrans is a radical chain process but the chain length is very small.

As reported in [1-4] the ratio [2]/[3] increases with increase in pressure. When $R = CH_3$ this increase is so great that to explain it either additions are made to the transformation scheme [2, 3] or it is postulated that the rates of formation of 2 and 3 are determined by the rate of rupture of the corresponding C-O bond in 1a; however, these rates depend in different ways on changes in the dynamic properties (viscosity) of the solvent with increase in pressure [4].

This question is fundamental enough for the present work to have been devoted to a more detailed study of the transformations of 1 (R = CH₃) and, for the first time, 1 (R = C₂H₅), including both compounds in benzene.



N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913. Translated from Izvestiva Akademii Nauk, Seriya Khimicheskaya, No. 4, pp. 822-828, April, 1992. Original article submitted February 11, 1991.

p, MPa	τ.h	[DTBP] ₀	[TBA]	[2]	[\$]	[2]/[3]
0.1	2	0.30	0 144	0.063	0.153	0.41
20	2 min	0.31	0.030	0.038	traces	-
20	10 min	0.29	0.033	0.046	0.011	4
20	0.5	0.29	0.048	0.038	0.051	0.74
20	2	0.30	0.139	0.051	0.111	0.46
20	3	0.5	0.41	0.137	0.40	0.34
20	7	0.30	0.307	0.118	0.285	0.41
20	30	0.29	0.587	0.234	0.66	0.35
100	2	0.30	0.114	0.065	0.114	0.57
100	3	0.65	0.304	0.134	0.40	0.33
100	Ť	0.30	0.26	0.103	0.25	0.41
200	3	0.65	0.30	0.16	0.40	0.40
250	2	0.30	0.096	0.046	0.082	0.56
250	7	0.30	0.194	0.075	0.166	0.45
300	3	0.65	0.20	0.091	0.24	0.38
400	3	0.65	023	0 134	0 274	0.49
500	2	0.30	0.05	0.03	0.034	0.87
500	3	0.64	0 136	0.094	0.164	0.57
500	7	0.30	0.136	0.05	0.105	0.47
750	2	0.30	0.04	0.025	0.023	1.1
750	7	0.30	0.101	0.031	0.034	0.91
1000	2	0.30	0.035	0.036	0.023	1.6
1000 *	2	0.29	0.020	0.053	0.015	3.5
1000	7	0.30	0.060	0.047	0.048	0.98
1000	30	0.29	0.251	0.065	0.155	0.42
1100		0.90	0.000	0.000	0.005	1.00

TABLE 1. Products of Homolytic Decompositions of 2-Methoxytetrahydropyran ($[1]_0 = 7.25-7.42 M$, 130°C, 0.08-0.41 M MB)

*Heated to 130°C at 1000 MPa.

EXPERIMENTAL

Experimental methods and analytical procedures for the products are as given in [5]. For GLC analysis of the reaction mixture the retention times of $3 (R = CH_3)$ and 2 were determined by the addition of known samples of these compounds to the mixture.

The concentrations of these compounds were determined by calibration against an internal standard, methyl benzoate (MB). The results of GLC analysis for TBA and 3 ($R = CH_3$) were in agreement with the NMR spectra, run on a Bruker WM-250 instrument. In addition, the formation of TBA, 2, and 3 ($R = CH_3$, C_2H_5) was confirmed by chromatography—mass spectrometry. No other substances were identified by these methods of analysis.

Synthesis of 2, which was needed for calibration, was effected by a new method: heating δ -chlorovaleric acid with a small excess of triethylamine for 3 h at 50°C under a pressure of 500 MPa. The yield was 90% of the initial acid by PMR. When the reaction was carried out at atmospheric pressure with other conditions the same, the yield was around 50% with considerable resin formation which made the isolation of 2 difficult.

Mathematical treatment of the experimental results by spline approximation of the corresponding curves was effected on an Elektronika-85 computer using the program of [6]. The number of discontinuities N and the values obtained for the standard deviation s are shown in the captions to the figures.

RESULTS AND DISCUSSION

According to the scheme set out above, the source of the formation of 2 and 3 is the radical 1a with the distinction that 2 is formed directly from 1a with elimination of R, while for the formation of 3 it is necessary that the linear radical 1b, obtained after rupture of the endocyclic C—O bond, should split off a hydrogen atom from the substrate molecule.

If the reaction were to take place only by these routes, then the ration [2]/[3] would be equal to the ratio of the rate constants for the rupture of the exocyclic and endocyclic C—O bonds. In principle, however, 1b can also be consumed by recombination with any radical present in the system with the formation of other products, thus breaking the chain, and in this case only a change in the rate of this particular chain-breaking step will influence the ratio [2]/[3]. A change in the rate of other reactions of radical compounds would result only in change of [1a]. Table 1 shows the data for the decomposition of DTBP in 1 (R = CH₃) at different reaction times τ and pressures p.





(For Figs. 1-5: Concentration M of δ -valerolactone 2 and the methyl and ethyl esters of valeric acid 3, their relative rates of formation, and the ratio [2]/[3] as functions of *tert*-butyl alcohol (TBA) concentration, 130°C.)

Fig. 1. 1 (R = CH₃), [DTBP]₀ = 0.30 and 0.65 *M*, p = 0.1-500 MPa: 1) shaded points, y = [2], RH axis, N = 4, s = 0.016; 2) unshaded points, y = [3], RH axis, N = 5, s = 0.041; 3) y = d[2]/d[TBA], LH axis; 4) y = d[3]/d[TBA], LH axis.

Fig. 2. 30 mole %, 1 (R = CH₃) and 70 mole % benzene, $[DTBP]_0 = 0.36 M, p = 20-1000$ MPa: 1) shaded points, y = [2], RH axis, N = 4, s = 0.017; 2) unshaded points, y = [3], RH axis, N = 4, s = 0.012; 3) y = d[2]/d[TBA], LH axis; 4) y = d[3]/d[TBA], LH axis. Fig. 3. 1 (R = C₂H₅), $[DTBP]_0 = 0.27 M, p = 20-1000$ MPa: 1) shaded points, y = [2], RH axis, N = 5, s = 0.018; 2) unshaded points, y = [3], RH axis, N = 5, s = 0.017; 3) y = d[2]/d[TBA], LH axis; 4) y = d[3]/d[TBA], LH axis.

Fig. 4. 30 mole %1 (R = C₂H₅) and 70 mole % benzene, [DTBP]₀ = 0.34 M, p = 20-1000 MPa: 1) shaded points, y = [2], RH axis, N = 3, s = 0.0087; 2) unshaded points, y = [3], RH axis, N = 5, s = 0.017; 3) y = d[2]/d[TBA], LH axis; 4) y = d[3]/d[TBA], LH axis.



Fig. 5. y = [2]/[3]: 1) 1 (R = CH₃), RH axis, N = 4; 2) 30 mole % 1 (R = CH₃) and 70 mole % benzene, LH axis, N = 4; 3) 1 (R = C₂H₅), RH axis, N = 4; 4) 30 mole % 1 (R = CH₃) and 70 mole % benzene, LH axis, N = 4.

We note that, in accordance with the experimental technique adopted, at all pressures the given temperature was attained at a minimum pressure of 20 MPa over 40 min and then, over 1.5-2 min, the pressure was increased to the required level. It was found that 5% of the peroxide reacted over this period and the formation of 2 predominated over that of 3. Increasing τ to 2 h at 20 MPa led to a sharp reduction in the ratio [2]/[3] after which it changed little.

Examination of the other results shows while the ratio [2]/[3] appears to be a function of τ , it is in fact a function of the extent of the conversion which can be expressed as the quantity of TBA formed. With increase in p the rate of decomposition of DTBP decreases and at 1000 MPa, after 2 h [TBA] = 0.035 M, i.e., it is four times less than [TBA] at 20 MPa in the same time, but the ratio [2]/[3], on the contrary, is four times greater in the first case than in the second. This ratio increases still further at 1000 MPa if heating to 130°C over 40 min is carried out not at 20 MPa as is usual, but at 1000 MPa, holding the temperature there for 2 h; the ratio [2]/[3] = 3.5 then becomes close to the value of [2]/[3] at p = 20 MPa and $\tau = 10$ min. The yields of TBA amount to 0.020 and 0.033 M, respectively. We note that in experiments carried out in absence of DTBP at 20 and 1000 MPa, 2 and 3 are either not detected at all or are formed in insignificant quantities.

The results presented provide evidence that comparison of the values of [2]/[3] at different p and the same $\tau = 2$ h, as was done in [1], leads to an incorrect conclusion regarding the considerable effect of p on the ratio [2]/[3]. In fact, such a comparison should be carried out at similar extents of conversion and this shows that [2]/[3] changes insignificantly with increase in p.

In Fig. 1, using results from all experiments (not only those in Table 1), [2] and [3] are plotted against [TBA] and curves 1 and 2 are constructed through these experimental points using the method of spline approximation. The first derivatives of the spline functions of 1 and 2 are also shown here as functions of [TBA] (curves 3 and 4), representing the relative rates of formation of 2 and 3, i.e., d[2;3]/d[TBA]. As can be seen, this rate is a wavelike function of the extent of conversion. At first, up to [TBA] = 0.1 M, d[2]/d[TBA] decreases by a factor of almost three but d[3]/d[TBA] changes little, which corresponds to the experimentally observed sharp decrease in [2]/[3] in this range of change in [TBA]. Then, the oscillations of both values approximately coincide in both phase and amplitude and the ratio [2]/[3] changes comparatively little.

These results relate to experiments at pressures p = 0.1-500 MPa and initial $[DTBP]_0 = 0.3$ and 0.65 *M* (32 points). Applying the spline approximation method to results obtained at p = 20 MPa and $[DTBP]_0 = 0.3$ *M* (17 points) gives a function similar to that of Fig. 1. These experiments were run up to complete decomposition of the DTBP (final [TBA] = 0.6 *M*). The results of calculations for experiments with p = 200-500 MPa and $[DTBP]_0 = 0.3$ and 0.65 *M* up to [TBA] = 0.3 *M* (13 points) also show a wavelike function for d[2;3]/d[TBA] against [TBA].

Results for experiments at 750 and 1000 MPa were not included in this series of calculations since a prolonged reaction time is required to achieve high conversions under these conditions. In addition, experiments at 1000 MPa and $\tau = 30$ h (Table 1) showed that [2] and [3] are markedly lower than the concentrations of these products at similar levels of conversion but at lower p. At the same time it proved possible to use results for the whole range of pressures up to p = 1000 MPa for other systems described below.

Figure 2 shows the functions for $1 (R = CH_3)$ in benzene. It can be seen that the oscillations of d[2]/d[TBA] and d[3]/d[TBA] are found in practically opposite phase over the whole range of conversions studied up to $[TBA] = 0.32 M (42\% \text{ on } [DTBP_b)$.

A different picture is observed in the case of $1 (R = C_2H_5)$ where the oscillations are synchronized and [2] is always greater than [3] (Fig. 3). Finally, in experiments with $1 (R = C_2H_5)$ in benzene, [2] is also greater than [3] but the synchronism of the oscillations of d[2]/d[TBA] and d[3]/d[TBA] is disturbed (Fig. 4).

All this is found to be in agreement with the observed changes in the ratio [2]/[3]. Figure 5 shows curves, calculated by spline approximation, for the experimental variation of [2]/[3] with [TBA]. As has already been noted, in the case of $1 (R = CH_3)$ the ratio [2]/[3] decreases over the range of change in [TBA] from 0.03 to 0.12 *M* by a factor of four — from 1.5 to 0.4 (curve 1). This decrease is more strongly marked in benzene (curve 2) — a factor of approximately 14 — after which for [TBA] = 0.21 *M* it increases by a factor of three. At the same time, in the case of 1 ($R = C_2H_5$) (synchronous oscillations of d[2]/d[TBA] and d[3]/d[TBA]) at the same extent of conversion, [TBA] = 0.12 *M*, the ratio [2]/[3] decreases over all by 20% and over the whole studied range of change in [TBA] (0.3 *M*) by approximately 30% (Fig. 5, curve 3). In the case of 1 ($R = C_2H_5$) in benzene, where the synchronism of the changes in d[2]/d[TBA] and d[3]/d[TBA] is considerably disturbed, a marked reduction in the ratio [2]/[3] is again observed as [TBA] increases — by a factor of two at [TBA] = 0.12 *M* and of three at [TBA] = 0.3 *M*.

Because of the weak relationship between the ratio [2]/[3] and the extent of conversion in the case of $1 (R = C_2H_5)$ there is no apparent significant effect of pressure on this ratio on comparing experiments with the same τ but with different extents of conversion. In the case of the three other systems studied, however, this effect is displayed to the same or a different extent. It should be noted that the overall rates d([2] + [3])/d[TBA], calculated from [2] + [3] as a function of [TBA] also, in general, show a wavelike change with increase in [TBA].

The results considered above are most probably explained by periodic change in the ratio of the reactivities of the radical **1a** to the rupture of the endocyclic and exocyclic C—O bonds and to the chain-breaking reaction in proportion to the accumulation of reaction products, i.e., change in the nature of the solvent.

As has already been noted, in the initial stage of the transformation the ratio [2]/[3] is quite high, especially in benzene. This result is convincingly confirmed in [7] where an analogous transformation of a large number of cyclic acetals was studied using photochemical initiation in the presence of benzophenone (BP). The reaction was carried out at $\sim 20^{\circ}$ C at atmospheric pressure, the initial acetal concentration in BP being 0.05 *M* in total which did not result in significant dilution of the benzene by the reaction products even up to 100% conversion of the acetal. In all cases, high values of [2]/[3] were observed, for example 16 for 1 (R = CH₃) and 14 for 1 (R = C₂H₅). Under our conditions in benzene, in the initial stages of the reaction these ratios were 8 and 4, respectively, but one should allow for the fact that the solvent here contained 70 mole % benzene and 30 mole % cyclic acetal and the reaction temperature was 100°C higher. On the other hand, in [8], after heating a mixture of 72 mole % 1 (R = CH₃) and 28 mole % DTBP at 120-130°C for 44 h, only TBA and 3 were found in the reaction mixture and generally 2 was not detected; here DTBP reacted to approximately 75% and 1 (R = CH₃) to 80%. A notable amount of product with molecular weight (MW) 412 was also detected, four times in excess of the MW of the initial 1 (R = CH₃).

Since, in the work of [8], the concentration $[DTBP]_0$ was almost ten times greater than that normally used in the present work, one can assume that both the composition of the solvent in the initial stage and the extent of its dilution by the reaction products on account of the differing rates of their formation are essentially different.

Thus, the results considered above are evidently explained by changes in the physical structure (dynamic properties) of the solvent, on the strength of which the reactivity of radical 1a toward rupture of the exocyclic and endocyclic C-O bonds also changes.

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