2-TERT-BUTYL PEROXIDE IN SOLUTION

V. M. Zhulin, I. Khuéidzha, E. B. Kabotyanskaya, and Yu. D. Koreshkov

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A study was carried out on the effect of pressure up to 1400 MPa on the homolytic decomposition of di-tert-butyl peroxide (DTBP) at 403 K in 2-methoxy- (I) and 2-ethoxytetrahydropyran (II) as well as in a mixture of 30 mole % (I) and 70 mole % benzene. Spline approximation of the experimental pressure dependence of the logarithm of the decomposition rate constant (k_d) gave the continuous dependence of the volumetric activation effect (ΔV^{\neq}) on pressure. The value of ΔV^{\neq} at atmospheric pressure (ΔV^{\neq}_0) and the nature of the change of ΔV^{\neq} with increasing pressure were found to depend on the nature of the solvent. This dependence is difficult to explain in the framework of the accepted transition state theory.

An increase in pressure in the liquid state, with rare exceptions, has an inhibiting effect on the decomposition of organic compounds with the formation of free radicals [1,2]. The magnitude of this effect in accord with the transition state theory is a function of the change in volume upon formation of the activated complex (ΔV^{\sharp}), which is positive in this case due to the increase in volume as a result of stretching of the bond to be broken in the activated complex.

le Noble represented the DTBP molecule as a cylinder and assumed that the extension of the 0-0 bond in the formation of the activation complex is 25%. This permitted estimation of ΔV_0^{*} at 6 cm³/mole [3]. Similar values of $\Delta V_0^{*} - 4.5$ cm³/mole were found in a study of organic peroxides and azo compounds, when we may assume that ΔV_0^{*} is a function of the extension of the bond to be broken upon formation of the activation complex. Values of ΔV_0^{*} have also been reported, which are several times greater than 4-5 cm³/mole. The concept of the cage effect is used to interpret such results but the experimental results cannot always be explained satisfactorily [1,2].

Preliminary data [4-6] show that the composition of the products of the radical conversion of 2-alkoxytetrahydropyrans initiated by tert-butoxy radicals arising in the decomposition of DTBP changes with increasing pressure, especially when 2-methoxytetrahydropyran is used. These results, which hold interest for development of the theory of the pressure effect on chemical processes, require more detailed experimental justification.

In the present communication, results are given for a study of the pressure effect on the rate of decomposition of DTBP in (I) and (II) as well as in a mixture of (I) and benzene.

EXPERIMENTAL

The starting 2-alkoxytetrahydropyrans were obtained from 2,3-dihydropyran and the corresponding alcohols according to the procedures described by Woods and Kramer [7]. Prior to use, the alcohols and benzene were purified [8] and distilled, while DTBP was only distilled. The purity of these samples was monitored by gas-liquid chromatography.

The experiments were carried out on a high-pressure cylinder piston apparatus [9] in 1-1.5 ml teflon ampuls. The pressure was measured on a manometer attached to the low-pressure chamber of the press with multiplication of these values by the ratio of the areas of the large and small pistons. A friction correction was not introduced. In all the experiments, the pressure was initially increased to 10-20 MPa. The sample

In all the experiments, the pressure was initially increased to 10-20 MPa. The sample was then heated and the temperature within the high-pressure insert containing the ampul was brought to 403 K. Reference experiments indicated that this took 40 min. Then, the pressure

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Fig. 1. Spline approximation of the experimental dependence of the logarithm of the rate constant for the decomposition of DTBP on pressure at 403 K in solvents: 1) (I), 2) (II), 3) 30 mole % (I) + 70 mole % benzene.

Fig. 2. Dependence of the volumetric activation effect for the decomposition of DTBP on pressure in solvents: 1) (I), 403 K, 2) (II), 403 K, 3) 30 mole % (I) and 70 mole % benzene, 403 K, 4) benzene, 393 K [12], 5) toluene, 393 K [12], 6) cyclohexene, 393 K [12].

was brought to the required level over not more than 1.5 min. The instant of achieving the required pressure was taken as the reaction onset.

The reaction mixture was analyzed by gas-liquid chromatography on an LKhM-80 chromatograph with a flame ionization detector on a 3 m \times 3 mm column packed with 5% Apiezon L on Inerton AW. The nitrogen gas carrier flow rate was 10 liters/h. The program was carried out at 2 deg/min. The calculation was carried out relative to methyl benzoate added as an internal standard. The conversion of DTBP was determined relative to the amount of tert-butyl alcohol (TBA) formed. The starting DTBP concentrations ranged from 0.26 to 0.36 M. Several experiments were carried out with concentrations twice or thrice those indicated.

Acetone may be formed in the decomposition of DTBP in addition to TBA, especially in experiments with a mixture of solvents containing benzene, which is inert as a proton donor. Under our chromatography conditions, the acetone peak was overlapped by the TBA peak, which was shown in experiments with added acetone. Thus, experiments were carried out, in which the reaction mixture was analyzed both by gas-liquid chromatography and PMR spectroscopy. When (I) was used as the solvent and the experiments were carried out at 20 and 1000 MPa over 30 h, acetone either did not form at all or was detected in only trace amounts. When a mixture of (I) and benzene was used as the solvent and the reaction was carried out over 7 h at 1000 MPa, acetone was also not detected, while this product is formed in small amounts at 20 MPa, which may be neglected in calculating k_d . The acetone content in the mixture with TBA was 23.9% at 20 MPa and 18.3% at 1000 MPa only in experiments with [DTBP]_0 = 1.1 M carried out over 30 h (the DTBP concentration was increased by decreasing the concentration of (I) and not of benzene). The value of k_d obtained taking account of the amount of acetone formed is close to its average value calculated using the results of the experiments carried out with lower DTBP concentrations and at shorter reaction times (2 and 7 h).

The experimental error given as the mean square deviation was 8-10% of the average \boldsymbol{k}_d value.

RESULTS AND DISCUSSION

According to the transition state theory

$$k = \varkappa \frac{kT}{h} e^{-\Delta G^{\neq}/RT}$$
⁽¹⁾

where k is the reaction rate constant, k and h are the Boltzmann and Planck constants, T is the absolute temperature, ΔG^{\neq} is the change in the Gibbs free energy upon the formation of

TABLE 1. Mean Experimental and Model Rate Constants for the Decomposition of DTBP in (I), (I)-Benzene, and (II) at 403 $K^{a,b}$

P, MPa	k _d . 10 ⁶ , sec ⁻¹					
	(I)	(I) + benzene	(II)C			
0,1 20 100 250 300 500 750 1000 1400	$\begin{array}{c} 38,1(1)/34,9\\ 33,1(4)/32,8\\ 24,7(3)/26,1\\ 19,4(4)/18,2\\ 15,4(1)/16,3\\ 11,1(5)/11,5\\ 8,6(4)/8,4\\ 6,7(6)/6,7\\ 5,3(1)/5,3\\ \end{array}$	-/26,9 27,0(4)/26,5 23,2(3)/23,8 19,0(3)/18,9 -/17,6 11,5(3)/12,6 9,1(5)/9,0 7,8(4)/7,8	$\begin{array}{r} -/46,8\\ 42,1(2)/41,9\\ 30,0(2)/33,1\\ 26,0(2)/23,8\\ -/21,7\\ 17,7(2)/17,4\\ 13,9(2)/15,4\\ 15,3(2)/14,4\\ 40,1(1)/10,3\\ \end{array}$			

^a[DTBP]₀ = 0.29-0.36 M; mixture of 2.66 M (I) in benzene. ^bThe experimental value for k_d is given in the numerator, while the model value is given in the denominator. The number of experiments carried out to obtain the mean value of k_d is given in parentheses.

"The duration of all the experiments using (II) was 5 h.

TABLE 2. Observed Volumetric Activation Effects for the Decomposition of DTBP (ΔV^{\neq}) in the Solvents Studied at 403 K and for Benzene, Toluene, and Cyclohexene at 393 K According to Buback [12]

	ΔV [;] , cm ³ /mole						
P.MPa	(I)	(I)+ ben- zene	(11)	ben- zene	toluene	cyclo- hexene	
0,1 400,0	10.5 5,2	3 ,9 5,6	11.5 3,8	13.1 9.9	7,9 5,0	8,1 7,2	
at $P=0.1$ MPa	34,9	26,9	46,8	12,9	13,4	8,4	

the activated complex, and κ is the transmission coefficient characterizing the probability of the transition of the activated complex to the reaction products.

The common use of Eq. (1) for reactions in the liquid phase is based on the assumption that $\kappa = 1$ and is independent of the thermodynamic state of the system such as pressure. In this case, taking the logarithm with subsequent differentiation of Eq. (1) relative to pressure taking account that $d(\Delta G^{\sharp})/dp = \Delta V^{\sharp}$ leads to well-known equation (2) [3]

$$\frac{d\ln k}{dp} = -\frac{\Delta V^{\neq}}{RT} \tag{2}$$

Equation (2) implies that ΔV^{\neq} may be found by differentiation of the dependence of $\ln k$ (or log k) on P.

In the present study, ΔV^{\neq} was calculated using the spline approximation method (SA) for the dependence of log k_d on P [10,11]. Approximation by a fourth-order spline function permits us to determine the value of ΔV^{\neq} and $(d\Delta V^{\neq}/dp)$ at any pressure in the range studied, i.e., obtain the continuous dependence of ΔV^{\neq} on P.

Table 1 gives the mean values of k_d and the values obtained using SA (model values). The experimental values of log k_d in Fig. 1 are plotted vs. P; the solid curves are drawn through the model values of log k_d . Figure 2 gives the dependence of ΔV^{\neq} on P obtained by the SA method (curves 1-3). This figure also shows curves calculated according to the SA method using the data of Walling and Metzger [12], who studied the decomposition of DTBP in benzene, toluene, and cyclohexene at 393 K. Figure 2 shows that the values of ΔV^{\neq}_0 and the change in ΔV^{\neq} with increasing pressure P depend significantly on the nature of the solvent. For clarity, Table 2 gives ΔV^{\neq}_0 and ΔV^{\neq}_p (P = 400 MPa). The ΔV^{\neq}_0 values for benzene and the

mixture of (I) and benzene differ by a factor of 3 but ΔV^{*} in both cases varies only slightly with increasing P up to 400 MPa.

This change is also slight for toluene and cyclohexene. On the other hand, the $\Delta V_{\alpha}^{\dagger}$ values for solvents (I) and (II) are similar to the ΔV_0^* values for benzene but are reduced by a factor of 2-3 at 400 MPa, while ΔV^{\neq} (benzene) decreases only by 25%. These discrepancies in ΔV^{\neq}_0 and the nature of the change in ΔV^{\neq} with increasing pres-

sure probably cannot be explained by the circumstance that the observed ΔV^{\sharp} value contains only a contribution from the change in volume upon the formation of the activated complex. The concept of the cage effect on the decomposition rate also is not useful. Furthermore, there is apparently no cage effect in the observed decomposition of DTBP. Buback and Lendle [13] drew this conclusion in a study of the decomposition of DTBP in heptane at 10, 120, and 230 MPa and 413-473 K. According to these results, $\Delta V^{\neq} = 10 \text{ cm}^3/\text{mole}$ and the activation energy E = 151.4 kJ/mole at all the pressures studied.

In considering decomposition reactions, the possibility of change in the transmission coefficient with increasing pressure must apparently be taken into account. These changes have received some theoretical justification in the stochastic model, which predicts the possibility of a different dependence of the reaction rate constant on the dynamic properties of the solvent. To a first approximation, such properties may be correlated with solvent viscosity [14].

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