- 3. M. E. Vol'pin and V. B. Shur, "Fixation of molecular nitrogen in aprotic media," in: New Trends in Chemical Nitrogen Fixation, Academic Press, London (1980), pp. 67-100.
- 4. E. Laviron, J. Besanson, and F. Hug, J. Organomet. Chem., <u>159</u>, 279 (1978).
- 5. Y. Mugnier, C. Moise, and E. Laviron, J. Organomet. Chem., 204, 61 (1981).
- Y. Mugnier, A. Fakhr, M. Fauconet, C. Moise, and E. Laviron, Acta Chim. Scand., <u>B37</u>, 423 (1983).
- 7. N. El Murr, A. Chaloyard, and J. Tirouflet, J. Chem. Soc. Chem. Commun., 446 (1980).
- 8. V. V. Strelets, G. L. Soloveichik, A. I. Sizov, B. M. Bulychev, A. Rusina, and A. A. Vlchek, Izv. Akad. Nauk SSSR, Ser. Khim., 2493 (1983).
- 9. A. N. Nesmeyanov and K. A. Kochetkov (eds.), Methods of Organometallic Chemistry. The Subgroup of Copper, Scandium, Titanium, Vanadium, Chromium, and Manganese. The Lanthanides and Actinides [in Russian], Vol. 1, Nauka, Moscow (1974), pp. 181, 323.
- 10. V. V. Strelets, S. V. Kukharenko, G. L. Soloveichik, A. N. Protskii, and A. Rusina, Izv. Akad. Nauk SSSR, Ser. Khim., 1484 (1985).
- 11. A. Fakhr, Y. Mugnier, R. Broussier, B. Gautheron, and E. Laviron, J. Organomet. Chem., <u>255</u>, C8 (1983).
- 12. H. P. Fritz, Adv. Organomet. Chem., <u>1</u>, 240 (1964).
- 13. V. V. Strelets and S. V. Kukharenko, Dokl. Akad. Nauk SSSR, 275, 894 (1984).
- 14. V. V. Strelets and S. V. Kukharenko, Nuov. J. Chim., 8, 785 (1984).
- 15. J. W. Lauher and R. Hoffmann, J. Am. Chem. Soc., <u>98</u>, 1729 (1976).
- S. Azavamuthan, C. Kalidas, and C. S. Venkatachalam, J. Electroanal. Chem., <u>171</u>, 293 (1984).
- S. Azavamuthan, C. Kalidas, and C. S. Venkatachalam, Ber. Bunsenges. Phys. Chem., <u>89</u>, 880 (1985).

BEHAVIOR OF ORGANIC PEROXIDES UNDER CONDITIONS OF HIGH PRESSURES AND SHEAR DEFORMATIONS

A. I. Dyatlov, A. A. Zharov, and V. M. Zhulin UDC 541.12.034.2:542.92:547.582.3

In deformation under high pressure, solid substances can enter into chemical reactions. Organic compounds can be polymerized, enter into Diels-Alder reactions, be added on the double bonds of molecules of H_2O and NH_3 , etc. [1, 2].

The transformations of peroxides during their shear deformation under high pressure (SD + HP) were studied in the present article. Benzoyl (I), lauryl (II), and cumyl peroxides (III), disuccinic acid peroxide (IV), and benzyldimethylsilyl peroxide (V) were investigated.

The studies showed that the degree of decomposition of the peroxides with SD + HP is a function of the pressure (Figs. 1 and 2), the degree of deformation (Fig. 3), and the temperature (Table 1, Fig. 4). Decomposition begins with some pressure (threshold pressure) characteristic of each peroxide (Fig. 1). Similar dependences were previously found in studying other reactions [1, 2] and were attributed to change in the conditions of deformation of the sample: with low pressures, the anvils initially slip along the sample, and the slipping stops and deformation involving the internal layers of the substance begins at some pressure [3], which results in the onset of chemical transformations of the substance.

The value of the shear stress is sensitive to the conditions of deformation of the substance [1]. For this reason, the above hypothesis can be tested with respect to the shape of the shear stress-pressure dependences, which should reflect the character of the movement of the substance on the anvils [3]. In addition, the movement of the substance during the SD + HP experiment can be studied by the colored pellet method [4].

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1028-1031, May, 1986. Original article submitted December 27, 1984.



Fig. 1. Dependence of the degree of decomposition of peroxides (in %) during deformation (140° angle of rotation of anvils, 6.9 mm anvil diameter, 20°C) on the pressure.

Fig. 2. Dependence of the shear stress (τ) on the pressure in decomposition of peroxides under conditions of SD + HP.

TABLE 1. Values of the Activation Energy (E_a) and Volume Effects of Activation (ΔV^{\neq}) for Peroxides with SD + HP and in Thermal Decomposition under Pressure in the Solid Phase and in Solutions

Peroxide	E_a (with SD + HP, p = 6 GPa), kJ/ mole	<i>E_a</i> (solid phase, p = 1.0 GPa), kJ/mole	E _a (liquid phase, p = 0.1 MPa), kJ/mole	$\Delta V \neq$ (with SD + HP, 293°K, p = 3-7 GPa) cm ³ / mole	∆V≠ (solid-phase thermal de- composition in the region of 0.01-1.5 GPz cm ³ /mole	∆V [≠] (liquid-phase thermal decom- position in the region of 0.01-1.0 GPa), cm ³ /mole
(I)	13,4±0,8 *	109,2±12	130,3 [6]	-1,3	2,0	5-9 [7, 8]
(II) (III) (IV)	$12,5\pm0,8$ $17,7\pm0,8$ $15,6\pm0,8$ -	$58,8\pm 6$ 27,3\pm 4 25,2\pm 6	130,7 [6] 142,9 [6] 169,8 [9]	-1,9 -1,3 -0,6	0,3 1,6 -2,0	-8, -10 [5]

*p = 4 GPa.

The results of measuring the shear stress (τ) are shown in Fig. 2. The points of the inflection in the τ -pressure curves correspond to the threshold pressure values (cf. Figs. 1 and 2).

The experiments with colored pellets showed that the time of movement of the boundary of the colored area of the sample is located in the pressure range where the beginning of decomposition of the peroxides occurs (see Fig. 1). These results thus confirm the hypothesis that the beginning of decomposition of the peroxide is due to the beginning of deformation of the substance in the bulk of the sample when a certain pressure is attained.

The degree of decomposition of the peroxides, particularly (I) and (II), increases with an increase in the deformation (see Fig. 3). Peroxide (I) decomposes with the formation of benzoic acid, phenol, phenyl benzoate, and a polymer; peroxide (II) decomposes with the formation of lauric acid, undecane, and decane; peroxide (III) decomposes into dimethylphenylcarbinol and a polymer; peroxide (IV) decomposes into succinic acid; and peroxide (V) decomposes into benzyl alcohol and oligomers.

The study of the thermal decomposition of the peroxides under conditions of static pressure with no shear showed that the organic peroxides decompose in the solid phase differently than in solutions in conditions of SD + HP and in thermal decomposition. In turn, the reac-



Fig. 3. Dependence of the degree of decomposition of (I) (%) on the deformation (θ) with p = 4 GPa and anvil rotation rate of 5.6 (1) and 105°/min (2).

Fig. 4. Logarithmic dependence of the rate constants of decomposition of (I) with SD + HP on the temperature at pressures of 4 (1) and 6 GPa (2).

tion of decomposition of the peroxides with SD + HP differs sharply from solid-phase thermal decomposition under static pressure. With SD + HP, diphenyl, usually found in the products of decomposition of this peroxide both at atmospheric and at high pressures, is absent in the products of decomposition of (I). At the same time, phenol and a significant amount of polymer, which are not present in the products of thermal decomposition, are present in the sample after SD + HP. SD + HP experiments were conducted in an atmosphere of Ar to determine the causes of the formation of phenol, and it was found that the amount of phenol formed decreased by several times in this case. It can thus be hypothesized that phenol is formed as a result of the reaction of the phenyl radicals generated from (I) with the oxygen in the air.

Organosilicon peroxide (V) also decomposes differently as a function of the experimental conditions. It is known that (V) is quantitatively rearranged into $C_6H_5CH_2Si(CH_3)_2OSi(CH_3)_2$. $CH_2C_6H_5$ when heated in solution under high pressure (1.4 GPa) [5]. The decomposition of (V) in the solid form at the same pressure results in products of rearrangement and homolytic decomposition (benzyl and organosilicon alcohols). Under conditions of SD + HP, no formation of a product of rearrangement is observed, and decomposition takes place with a formation of alcohols.

The difference in the decomposition of the peroxides as a function of the experimental conditions is also found in the effect of pressure. Slowing of the reaction with an increase in the pressure is usually observed in the decomposition of peroxides in solutions. In the solid phase, the retarding effect of the pressure is also characteristic. Only (V) is an exception. The process of decomposition of the peroxides under conditions of SD + HP is accelerated in all cases with an increase in the pressure, and the volume effects of activation are negative (see Table 1).

The decomposition of the peroxides with SD + HP was studied in a wide range of temperatures. The temperature coefficients of the reactions of decomposition of the peroxides with SD + HP, expressed as the values of the activation energies for clarity, and the activation energies of the peroxides in other conditions are reported in Table 1. It can be seen that the decomposition of the peroxides with SD + HP is significantly less dependent on the temperature than in thermal decomposition both with and without pressure. In the case of (I), the temperature coefficient determined at 4 and 6 GPa does not vary with the pressure within the limits of the experimental errors (see Fig. 4).

The differences in the chemical process with SD + HP from the reactions which take place in solutions and in the solid phase thus consist of a different qualitative and quantitative composition of the products of decomposition, significantly lower temperature coefficients, and volume effects of activation which differ in sign.

EXPERIMENTAL

The experiments with SD + HP were conducted on an anvil apparatus [1] at pressures of up to 8000 MPa and temperatures from -80 to 60° C. The decomposition of the solid peroxides with the effect of high pressures (up to 1.5 GPa) alone was studied on an apparatus of the cylinder-piston type. The solid peroxides were pressed into pellets 12 mm in diameter and 0.1 mm thick, which were separated from the metal walls of the apparatus by a layer of Teflon. Peroxides with a purity greater than 98% were used. The amount of undecomposed peroxide was determined by iodometric titration [10]. The products of decomposition of the peroxides were analyzed by GLC using column packed with 5% silicone SE-30 and XE-60 on Chromaton N-AW-DMCS.

CONCLUSIONS

1. The deformation process of decomposition of peroxides fundamentally differs from the thermal decomposition of peroxides in the solid phase and in solutions both at atmospheric and at high pressure.

2. The basic features of the chemical decomposition of the peroxides with shear deformation under high pressure are: the high rate, dependence of the degree of transformation on the value of the deformation, low-temperature coefficient, and different composition of the products of decomposition than in thermal decomposition of the peroxides in the solid phase and in solutions under atmospheric and high pressures.

LITERATURE CITED

- 1. A. A. Zharov, Dissertation, Moscow (1979).
- V. S. Abramov, A. A. Zharov, V. M. Zhulin, and G. P. Shakhovskoi, Izv. Akad. Nauk SSSR, Ser. Khim., 1462 (1978).
- 3. A. G. Kazakevich, A. A. Zharov, P. A. Yampol'skii, and N. S. Enikolopyan, in: Mechanoemission and Mechanochemistry of Solids [in Russian], Ilim, Frunze (1974), p. 247.
- V. A. Zhorin, A. A. Zharov, A. G. Kazakevich, and N. S. Enikolopyan, Fiz. Tverd. Tela, <u>17</u>, 393 (1975).
- 5. V. A. Yablokov, A. V. Ganyushkin, M. Ya. Botnikov, and V. M. Zhulin, Izv. Akad. Nauk SSSR, Ser. Khim., 484 (1978).
- N. K. Nikhon Yuushii, List of Organic Peroxides [Russian translation], Tokyo (1975), p. 21.
- 7. G. Walling and J. Pellon, J. Am. Chem. Soc., 79, 4789 (1957).
- 8. A. E. Nicholson and R. G. W. Norrish, Disc. Faraday. Soc., 22, 9 (1956).
- 9. A. P. Mar'in, V. A. Yablokov, A. N. Sunin, and Yu. A. Shlyapikov, Izv. Akad. Nauk SSSR, Ser. Khim., 2251 (1975).
- R. M. Johnson and I. W. Siddigi, The Determination of Organic Peroxides, Pergamon Press, New York (1966), p. 126.