

Kinetics of the decomposition of benzoyl peroxide in poly(methyl methacrylate) at high pressures

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Investigating the influence of pressure on the rate of the thermal decomposition of benzoyl peroxide in poly(methyl methacrylate) at 100°C, a reaction rate decrease with pressure over the range $2 \times 10^3 - 8 \times 10^3$ kp cm^{-2} was observed, the found value of the activation volume of this process being $7.5 \text{ cm}^3 \text{ mol}^{-1}$.

Studying the kinetics of the decay of macroradicals generated by a thermal decomposition of benzoyl peroxide in poly(methyl methacrylate) at high pressures [1] a phenomenon was observed indicating a retardation effect of the pressure not only on the proper interaction of polymer radicals but also on their formation process, *i.e.* on the very thermal decomposition of the peroxide. This assumption was confirmed by a direct experimental evidence [2]: at 10^4 kp cm^{-2} , the half-life of benzoyl peroxide in such a system has, even at 150°C, the same value (~ 10 min.) as at atmospheric pressure over the range 110–120°C.

To obtain quantitative data of the retardation effect of the pressure on this reaction, also the extent of its effect was investigated by determining the rate constants of the decomposition process in dependence on pressure over the range $2 \times 10^3 - 8 \times 10^3 \text{ kp cm}^{-2}$ at 100°C.

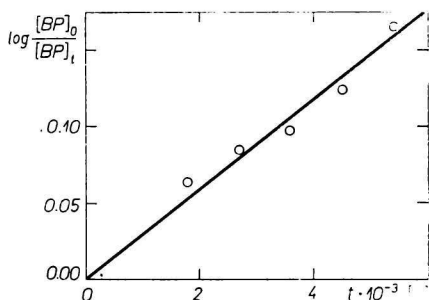


Fig. 1. Logarithm of the ratio of the initial concentration of benzoyl peroxide ($[BP]_0 = 0.052 \text{ mol kg}^{-1}$) and its concentration after decomposition ($[BP]_t$) in poly(methyl methacrylate) at 100°C and $2 \times 10^3 \text{ kp cm}^{-2}$ in dependence on time (t).

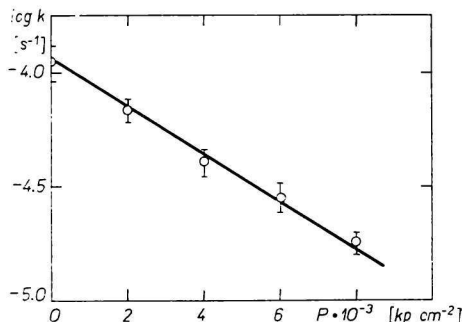


Fig. Logarithm of the rate constant of unimolecular decomposition of benzoyl peroxide in poly(methyl methacrylate) vs. pressure at 100°C.

From the results of the decomposition of benzoyl peroxide in poly(methyl methacrylate) at 100°C and 2×10^3 kp cm⁻² (Fig. 1) it follows that, though at lower temperature (80°C) the considered reaction seems to be of chain character [3], under the experimental conditions a decomposition that might be induced parallelly with the spontaneous process could not be observed any more. This may probably be due to the relatively low share of the chain reaction which, with regard to the higher temperature and lower peroxide concentration, is overlapped by the scattering of the measured values.

For this reason the kinetics of the decomposition process was characterized by the rate constant of a unimolecular reaction, determined at the pressure of 2×10^3 kp cm⁻² from the time course of the decomposition reaction (Fig. 1) and at other pressures, only from parallel measurements of peroxide loss after the elapse of only one reaction period (Table 1). (Reaction times for individual pressures were chosen so as to prevent the peroxide loss from exceeding 30% of the starting value.)

Table 1

Concentrations of benzoyl peroxide after its decomposition ($[BP]_t$) at 100°C and at different pressures. (The initial concentration of peroxide was 0.052 mol kg⁻¹ in all cases.)

Pressure [kp cm ⁻²]	Reaction time $\times 10^{-3}$ [s]	$[BP]_t$ [mol kg ⁻¹]
1	2.4	0.040
4000	5.4	0.042
6000	14.4	0.034
8000	14.4	0.040

The data $[BP]_t$ are average values calculated from at least three parallel measurements.

Consequently an increase of pressure leads to a gradual decrease of the decomposition rate of benzoyl peroxide in poly(methyl methacrylate) which, when expressed as the logarithm of the rate constant *vs.* pressure (Fig. 2), has a practically linear course over the investigated range. The activation volume (ΔV^\ddagger) of this process calculated from the slope of the straight line obtained according to the equation [4]

$$\frac{\partial \ln k}{\partial P} = - \frac{\Delta V^\ddagger}{RT}$$

expressing the dependence of the rate constant of a general reaction on pressure (P), has then a positive value $\Delta V^\ddagger = 7.5$ cm³ mol⁻¹. This somewhat higher numerical value ΔV^\ddagger , when compared to the activation volume indicated for elementary cleavage processes of a single chemical bond (up to 5 cm³ mol⁻¹ [5]) may be explained also by the indirect influence of pressure, namely *via* an increase of viscosity [6] of the decomposition medium. This viscosity increase, which accentuates the reverse recombination of the primary radical pairs caused by the cage effect [7], will still increase the overall retardation effect of pressure.

Experimental

The benzoyl peroxide used was purified by threefold precipitation from its chloroform solution with methanol, whereas the purity of the product determined analytically reached 99.8%.

Pure methyl methacrylate was obtained by depriving the monomer of the last traces of polymerization impurities according to a usual procedure [8].

Poly(methyl methacrylate) samples containing benzoyl peroxide were prepared by dissolving the required amount of peroxide in monomer and by its polymerization in glass tubes (sealed in nitrogen atmosphere), tempered for 70 hours in a thermostated water bath at 30°C. The peroxide concentration in the final polymer was checked analytically.

From poly(methyl methacrylate) blocks prepared by the above procedure, cylindrical samples (length and diameter 6 mm) were turned out. The proper tempering of samples under pressure was carried out so that they, after having been inserted into a hollow steel cylinder (inner diameter 6 mm), were compressed by a piston to the required pressure and quickly heated to 100°C. The constant tempering conditions were obtained by temperature and pressure stabilization (temperature deviations being in the range $\pm 2^\circ\text{C}$ and those of pressure $\pm 100 \text{ kp cm}^{-2}$). After elapse of the reaction time the press mould was rapidly cooled down and the pressure released. The time necessary for samples heating and cooling was negligible with respect to the tempering period. The content of undecomposed benzoyl peroxide was isolated from the tempered samples — after their disintegration — by an 8-hour extraction with boiling methanol. In the extract obtained, the peroxide was determined by titration of iodine (with a 0.01 N solution of sodium thiosulfate), released from potassium iodide in the medium of glacial acetic acid at laboratory temperature [9].

References

1. Szőcs, F., Plaček, J., and Borsig, E., *J. Polym. Sci.* **B9**, 753 (1971).
2. Rado, R. and Szőcs, F., *Vysokomol. Soedin.* **B14**, 564 (1972).
3. Rado, R., *Chem. Zvesti* **19**, 46 (1965).
4. Bamford, C. H. and Tipper, C. F. H., *The Theory of Kinetics*, p. 316. Elsevier, Amsterdam, 1969.
5. Neuman, R. C. and Amrich, M. J., *J. Amer. Chem. Soc.* **94**, 2730 (1972).
6. Kuss, E. and Pollmann, P., *Z. Phys. Chem.* **68**, 205 (1969).
7. Ivanchev, S. S., Skubilina, L. V., and Denisov, E. T., *Vysokomol. Soedin.* **B9**, 706 (1967).
8. Burnett, G. M., *Mechanism of Polymer Reactions*, p. 13. Interscience, New York, 1954.
9. Antonovskii, V. L., Matalets, B. I., Golysheva, G. P., and Terentiev, V. A., *Khimiya perekisnykh soedinenii.* (Chemistry of Peroxidic Compounds.) P. 219. Izd. Akad. Nauk SSSR, Moscow, 1963.

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