Decomposition of Benzoyl Peroxide on the Synthetic Faujasite of the Na X Type

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The ESR method has been used for the measurement of the concentration-
-time dependence of the paramagnetic particles arising in the micropores of
the synthetic Na X faujasite after the adsorption of benzoyl peroxide from
benzene or methacrylic acid by heating the sample to the temperatures rang-
ing from 70°C to 100°C.

It has been found that the values of the rate constants k' corresponding to
the formation of stabilized radicals for the benzoyl peroxide adsorbed from
benzene at the temperatures between $80-100°C$ are $1 \times 10^{-3} - 3 \times 10^{-3}\,\text{s}^{-1}$
approximatively while the value of this constant for the benzoyl peroxide
adsorbed from methacrylic acid is $k = 1.4 \times 10^{-4}\,\text{s}^{-1}$ at 90°C.

The particles caught in the microstructure of zeolite are stable even at the
temperatures high above 100°C (140°C).

The porous microstructure of synthetic zeolites is known to have a stabilization
effect on the reactive free radicals [1]. Low temperatures at which most investigations
have been made up to now restrict the use of photochemical or radiation techniques
since the radical production is often accompanied by the formation of the para-
magnetic centres in the crystal structure of zeolite. The thermal methods of the
stabilized radical generation are thus applicable only to some suitable types of
adsorbed compounds.

For instance, it has been found out that benzoyl peroxide gives a relatively intense
ESR signal provided it has been adsorbed from benzene at room temperature and
subsequently heated over 50°C. After the readsorption by a monomer (*e.g.* metha-
crylic acid and its esters are suitable) this signal turns into the ESR spectrum of the
radicals corresponding to the initiation reaction of benzoyl peroxide with relevant
monomer [2].

On the basis of this conclusion, we decided to start with the study of kinetics of
the stabilized radicals formation to obtain fundamental information on the stabili-
zation mechanism on zeolites at higher temperatures regarding the possibility to
apply this technique to the investigation of chemical properties of the isolated
radicals of oligomer or polymer character.

Experimental

Benzoyl peroxide and methacrylic acid were purified in the usual way. The purity of benzene and methacrylic acid was tested by gas chromatography. The content of impurities did not exceed 0.5 volume %.

The activated granulated faujasite of the Na X type (commercial mark Nalsit 13) was prepared in the Research Institute of Petroleum and Hydrocarbon Gas in Bratislava. The molar ratio $SiO_2 : Al_2O_3$ in this zeolite was 2.5, the effective diameter of pores 9 Å and the diameter of granules $1-2$ mm. The ESR spectra were measured by means of the ESR spectrometer RE 1301, made in U.S.S.R.

Before each experiment the faujasite was reactivated by two hours' heating at 400°C in vacuum of 10^{-3} Torr. The solutions of benzoyl peroxide in monomer and benzene used for adsorption were prepared in the atmosphere of purified nitrogen at room temperature. Adsorption itself took place for 30 minutes at 27°C. To prepare the benzoyl peroxide—Na X system, benzoyl peroxide was adsorbed from a benzene solution by the zeolite and afterwards, benzene was distilled off at reduced pressure and room temperature. In this way, the adsorption isotherm for the adsorption of benzoyl peroxide from benzene was found, too. An equation $N_a = 1.75 \cdot c$ is valid for the concentration range of benzoyl peroxide in benzene from 1×10^{-4} to 4×10^{-4} mole per gram of solution at 27°C; N_a and c being the adsorbed amount of benzoyl peroxide in mole per gram of zeolite and the benzoyl peroxide concentration in benzene solution in mole per gram of solution, respectively. In the case of the parallel adsorption of benzoyl peroxide by methacrylic acid, the samples were cooled down with dry ice during the evacuation.

The ampoules with the benzoyl peroxide—Na X (eventually benzene or methacrylic acid) system were sealed and heated to a certain temperature in the resonator cavity of the ESR spectrometer.

Concentrations of free radicals were determined by comparing the area of the spectrum measured with that of a carbon standard.

Evaluation of results

The rates of the paramagnetic particle formation were characterized in both cases approximatively by the kinetic first order schemes which agree relatively well with experimental results
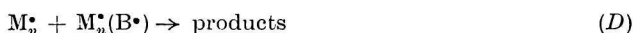
$$[B^+] = [B_\infty^+] \, (1 - e^{-k't}) \qquad (1)$$

or

$$[M_n^+] = [M_{n\infty}^+] \, (1 - e^{-kt}) \qquad (2)$$

where $[B^+]$ denotes the concentration of stabilized radicals arising after the adsorption of benzoyl peroxide on zeolite given in mole per gram of zeolite, $[M_n^+]$ is the concentration of stabilized oligomer or polymer radicals in mole per gram of zeolite, $[B_\infty^+]$ and $[M_{n\infty}^+]$ are the equilibrium concentrations for time $t = \infty$, k and k' are the rate constants of radical formation and t denotes time in seconds. The constants k and k' may be determined from the linear section of the relationship between $\log\{[B_\infty^+] - [B^+]\}$ or $\log\{[M_{n\infty}^+] - [M_n^+]\}$ and time since the slope of these relationships are $s = -k' \cdot \log e$ or $s = -k \cdot \log e$, respectively.

Results and Discussion

Provided the monomer is adsorbed as firmly as the peroxide in the simultaneous adsorption of monomer and benzoyl peroxide, it may be supposed that the movement of radical centre on the surface of zeolite is likely to have the mechanism involving the subsequent stages

$$BP \xrightarrow{\ k_1\ } 2B\bullet \qquad\qquad (A)$$

$$B\bullet + nM \xrightarrow{\ k_2\ } M_n^{\bullet} \qquad\qquad (B)$$

$$M_n^{\bullet} + S \xrightarrow{\ k_3\ } M_n^{+} \qquad\qquad (C)$$

$$M_n^{\bullet} + M_n^{\bullet}(B\bullet) \rightarrow products \qquad\qquad (D)$$

where BP, B•, M, $M_n^{\bullet}$, M_n^{+}, and S denote benzoyl peroxide, benzoyloxy radical, monomer, polymer radical, stabilized $M_n^{\bullet}$ radical, and stabilizing place on the surface of zeolite, respectively.

The constant k_2 reaches the value of 10^2 l mole^{-1} s^{-1} [3] at room temperature while the slowest step is the reaction (A) which controls the rate of stabilized radical formation.

These assumptions are really valid for the benzoyl peroxide and methacrylic acid (Table 1a). The rate constants of the stabilized radical formation k possess the values which are close to those of the rate constants of benzoyl peroxide decomposition in solution determined by other methods [3]. Some typical curves for the formation of polymer radicals from methacrylic acid and benzoyl peroxide are shown in Fig. 1.

These relationships do not start from the origin of coordinates because a certain amount of the stabilized particles arises even during the sample preparation at room temperature.

Table 1

Rate constants of the formation of the stabilized paramagnetic particles on the Na 13 X zeolite for a) benzoyl peroxide and methacrylic acid and b) benzoyl peroxide and benzene

	T [°C]	Amount of zeolite [g]	Concentration of benzoyl peroxide in monomer [mmole g^{-1}]	$k' \times 10^4$ [s^{-1}]	$k^* \times 10^4$ [s^{-1}]
a)	90	0.0217	0.136	1.40	
	90	0.0283	0.093	1.86	
	100	0.0398	0.082	3.92	
b)	70	0.0201	0.310	16.90	0.10
	80	0.0412	0.417	26.40	0.36
	90	0.0305	0.417	23.40	1.13
	100	0.0311	0.417	23.40	4.48

The k^* constants were calculated according to the Arrhenius equation for the decomposition of benzoyl peroxide in benzene solution in the absence of zeolite.

The dependence of the $[M_{n\infty}^+]$ concentration on equilibrium level with temperature points out that this quantity is a function of the surface structure of zeolite, of the particular constants k_1, k_2, k_3 or the initial concentration of benzoyl peroxide adsorbed. For the adsorption of benzoyl peroxide from benzene, the measured constants of the formation of stabilized paramagnetic particles are essentially greater (Table 2 and 1b). Provided the peroxide is adsorbed in several localized layers it is established
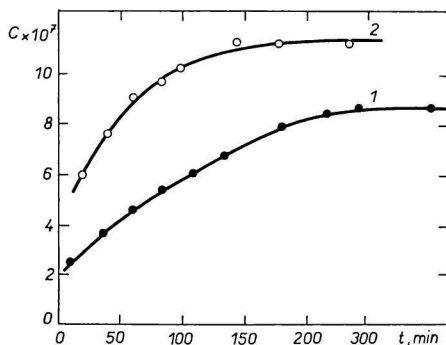

Fig. 1. Kinetic curves for the formation of paramagnetic particles in the system benzoyl peroxide—methacrylic acid—synthetic Na X faujasite.
1. $T = 90°C$; *2.* $T = 100°C$ (see Table 1a).
C is given in mole per gram of zeolite.

Table 2

Rate constants of the stabilized radicals formation from benzoyl peroxide on the Na 13 X zeolite

T [°C]	Amount of zeolite [g]	Concentration of benzoyl peroxide in benzene solution [mmole g^{-1}]	$k' \times 10^4$ [s^{-1}]
70	0.0223	0.426	3.09
70	0.0277	0.223	3.55
80	0.0249	0.340	13.80
80	0.0264	0.467	12.50
90	0.0200	0.536	11.60
90	0.0254	0.490	10.00

that the movement of a radical centre into a stabilizing pore is able to cause an induced decomposition. Let us assume again that the total process starts with the reaction (A), *i.e.*

$$\text{BP} \xrightarrow{k_1} 2\text{B·} \qquad (A)$$

$$\text{B·} + \text{BP} \xrightarrow{k_5} \text{B·} + \text{C} + \text{D} \qquad (E)$$

$$\text{B·} + \text{B·} \xrightarrow{k_6} \text{C} + \text{D} \qquad (F)$$

$$\text{B·} + \text{S} \xrightarrow{k_7} \text{B}^+ \qquad (G)$$

C, D being the products of benzoyl peroxide decomposition while B$^+$ is the stabilized radical B·. The B$^+$ radicals need not be principally benzoyloxy radicals, they may also be the products of the reactions between the phenyl radicals arising in the course of benzoyloxy radical decarboxylation and the non-radical products of benzoyl peroxide decomposition. The M_n^+ and B$^+$ radicals are then fixed in suitable pores in such a way that the mobile radicals have no access to them.

The experimentally established constants k and k' must therefore have a complex character. Because of the preferential adsorption of monomer, the constant k bears directly upon the spontaneous decomposition of benzoyl peroxide in solution. For the present, the constant k' is assumed to depend on the surface structure of zeolite, the constant of induced decomposition, the constant of spontaneous decomposition and on the initial amount of the adsorbed benzoyl peroxide or the termination rate constants of particular radicals.
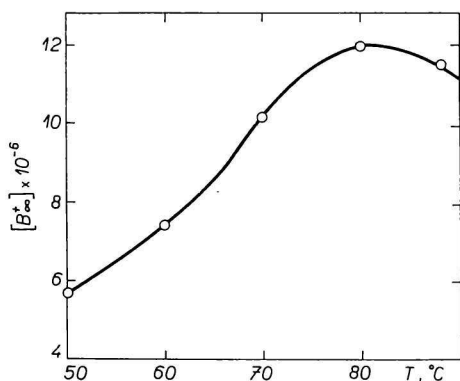

Fig. 2. Dependence of the equilibrium level of the radicals arising from benzoyl peroxide in the Na X zeolite on temperature. The [B$_\infty^+$] concentrations are expressed in millimetres of the ESR signal and related to 1 gram of zeolite and unit concentration of benzoyl peroxide in the solution in which adsorption has occurred.

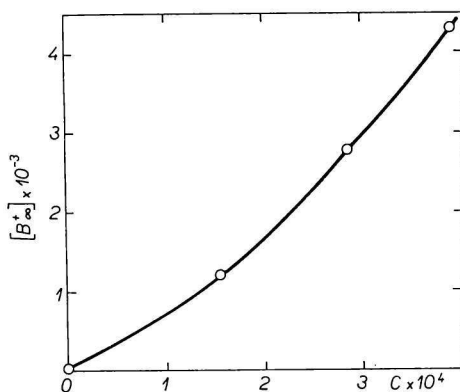$c = 1.9 \times 10^{-4}$ mole per gram of solution.

Fig. 3. Dependence of the equilibrium level of the radicals on the benzoyl peroxide concentration in the benzene solution. The radicals are formed in the Na X zeolite from benzoyl peroxide at 80°C. [B$_\infty^+$] is given in millimetre of the ESR signal per gram of zeolite.

From the Tables 2 and 1b it is evident that the rate constant k' evaluated in the described way does not depend on temperature according to Arrhenius equation. It is worth noticing that the value of k' passes the maximum value approximatively at equal temperature as the value of [B$_\infty^+$] (Fig. 2).

A kinetic evaluation of the results is very much impeded by the fact that it is hardly possible to determine the initial concentration of the adsorbed benzoyl peroxide supposing its homogeneous dispersion on the surface of zeolite. A certain homogeneity of the adsorbed benzoyl peroxide might exist in case of the simultaneous adsorption with methacrylic acid since the molecules of the acid preferentially occupy particular pores and make agglomerates in the force field of adsorbent easier than

the benzoyl peroxide molecules. We assume that the decomposition of the benzoyl peroxide following its adsorption from benzene is similar to its decomposition in solid phase with the only difference that the structure of zeolite has a catalytic effect and decreases the temperature necessary to reach the chain mechanism of the reaction.

The dependence of $[B_\infty^+]$ on temperature at a constant concentration of benzoyl peroxide in solution as well as that of $[B_\infty^+]$ on the concentration of benzoyl peroxide in solution at constant temperature possesses a peculiar character (Figs. 2 and 3). The maximum at about 80°C (Fig. 2) may be interpreted by the circumstance that the kind of benzoyl peroxide adsorption may vary with varying mobilities of the
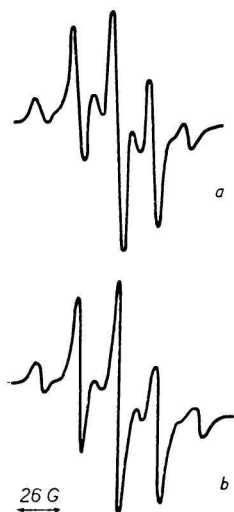

Fig. 4. ESR spectra of radicals.
a) Radicals prepared by mechanical destruction of polymethyl methacrylate at liquid nitrogen temperature. Temperature of measurement 40°C.
b) Radicals prepared by thermal decomposition of benzoyl peroxide in methacrylic acid on the Na X zeolite at 90°C. Temperature of measurement 40°C. Concentration of particles was in both cases 5×10^{17} spin per gram of sample.

adsorbed particles and with increasing possibility of the mutual recombination of radicals during the formation of the decomposition products such as diphenyl, phenyl benzoate, *etc.* It is possible that benzene plays an important role because small amounts of this substance may remain occluded together with benzoyl peroxide in zeolite. The values of the k' constants in Table 1b support this idea.

The dependence of $[B_\infty^+]$ on the concentration of benzoyl peroxide in solution is in principle a function of the structure of zeolite and of the constants influencing the chemism of benzoyl peroxide decomposition.

The stabilizing effect of zeolite on free radicals is to be corroborated by the following experiment: If the reactivated zeolite is exposed to the effect of air humidity and subsequently benzoyl peroxide is adsorbed, the yields of radicals obtained fall to 1/5—1/10 of the original values. Provided the humidity is effective for another period of time, no ESR spectrum of corresponding radicals can be obtained even after several hours' heating of the sample at 100°C. The amount of adsorbed water is so small in this case that it does not influence the quality of the cavity resonator at all. The reproducibility of results is then very poor from the kinetic point of view.

The ESR spectrum of the radicals arising in the course of benzoyl peroxide decomposition in the absence of monomer is a singlet which has the line width $\Delta H_{1/2} = {} = 11.8$ gauss at 70°C ($g \approx 2.004$).

Zeolite itself does not give any ESR signal even at the highest sensitivities of the instrument.

In Fig. 4 the differences between the ESR spectra of the radicals prepared from methacrylic acid by thermal decomposition and those obtained by mechanical destruction of the polymethyl methacrylate sample at the temperature of liquid nitrogen are presented. Both spectra are recorded at 40°C. The differences in heights of the second, fourth, sixth, and eighth line may be interpreted by various proportions of several types of radicals.

The kinetic study of the benzoyl peroxide decomposition on synthetic zeolites shows the character of adsorption forces in the benzoyl peroxide—zeolite system as well as on the proper decomposition of benzoyl peroxide or the catalytic properties of adsorbent [4]. If we take into consideration the dimensions of the micropores in zeolite which are responsible for a certain selectivity in the stabilization of radicals according to their size, it is evident that the kinetic curves provide us a complex view on the total problem. It is, however, difficult to decide immediately whether the adsorption and thermal decomposition are consecutive processes or whether the adsorption itself must involve the decomposition of benzoyl peroxide. The substances occurring in the equations $(A-G)$ are in an adsorption—desorption equilibrium on the surface of zeolite. But in the course of the benzoyl peroxide decomposition some products are formed which are adsorbed less firmly (e.g. diphenyl) and will diffuse outwards from inside particular pores of the microstructure of zeolite. An opposite tendency is to be expected with the more polar decomposition products (e.g. phenyl benzoate).

All these factors effect the resulting kinetic relationships. The presence of monomers changes the adsorption on zeolite in such a degree that the catalyzed decomposition may be inhibited.

Regardless the complications due to the interpretation of kinetic relationships, this method is quite suitable for the preparation of sufficient concentrations of the isolated C radicals arising during the radical polymerization of methacrylic acid and its esters. We suppose that it will be possible to study the properties of these radicals in more details and in particular, to investigate their interaction with oxygen and their depolymerization reactions over the temperature range from 0°C to 100°C as well.

References

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