Induced decomposition of 9,10-dioxyanthracene

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Thermal decomposition of photoperoxide of anthracene in solvents such as naphthalene, 2-bromonaphthalene, and methyl methacrylate and at temperatures from 90 to 150°C proceeds almost exclusively by induced mechanism with activation energy 120 kJ mol^{-1}. Rate constant of induced decomposition is at 120°C about two orders higher than that for spontaneous decomposition. For peroxide concentration above 0.2 mol dm^{-3} induced decomposition is of the first order. This makes difficult to distinguish it from spontaneous reaction which is also of the first order. At the decrease of initial concentration of decomposing 9,10-dioxyanthracene the order of induced decomposition changes to 1.5.

The consequences of induced decomposition with regard to initiation power of anthracene peroxide in polyreactions and thermal sensitivity of its decomposition in the solid state are discussed.

Thermal decomposition of 9,10-dioxyanthracene was investigated by means of calorimetry and chemiluminescence method.

Термическое разложение фотоперекиси антрацена происходит в растворителях (нафталин, 2-бромнафталин, метилметакрилат) при температуре 90—150°C почти исключительно по механизму индуцированного разложения с энергией активации 120 кДж моль^{-1}. Константа скорости индуцированного разложения при 120°C на два порядка выше, чем константа скорости спонтанного распада. Индуцированный распад при концентрации перекиси больше, чем 0,2 моль дм^{-3} является реакцией первого порядка, что затрудняет его отграничение от спонтанного разложения того же порядка. Порядок реакции индуцированного разложения превышает единицу только при понижении концентрации разлагающейся циклической перекиси антрацена.

Обсуждается влияние индуцированного разложения на эффективность инициирования реакций полимеризации и термическую чувствительность разложения перекиси в твердом состоянии.

Термическое разложение 9,10-диоксиантрацена изучалось при помощи дифференциальной калориметрии и хемилюминесценции.

Until now, thermal decomposition of 9,10-dioxyanthracene was evaluated quantitatively either from the rate of initiation of styrene polymerization [1] or from measurements of the rate of heat evolution during the decomposition [2].

First-order rate constants of decomposition reaction were determined from the amount of polystyrene formed under standard conditions of polymerization (70°C, 1 h) carried out after foregoing partial thermal decomposition of 9,10-dioxyanthracene in benzene. It was ascertained by this method that the thermal decomposition in dioxan was twice and in ethyl acetate ten times faster than in benzene. This was accounted for by induced decomposition of 9,10-dioxyanthracene. Since the rate of decomposition was determined only for one value of initial concentration of 9,10-dioxyanthracene the role of induced decomposition in overall process when compared to spontaneous one cannot be assessed even approximately.

Calorimetric measurements of decomposition rates in naphthalene were carried out at about 30 times higher concentration of 9,10-dioxyanthracene than those in benzene reported in preceding paper [1]. Even in that case similar kinetic parameters of decomposition reaction were attained (activation energy 125 kJ mol^{-1}, preexponential terms in Arrhenius equation $1.5\times10^{14}\ \mathrm{s}^{-1}$ [1] and $5\times10^{14}\ \mathrm{s}^{-1}$ [2], respectively). Taking into consideration the above-mentioned results the thermal decomposition of this transannular cyclic peroxide in aromatic hydrocarbons may be assumed either as monomolecular reaction with an insignificant part of induced decomposition or as induced chain process of the first order coinciding with monomolecular spontaneous reactions. At the same time, low initiation efficiency of 9,10-dioxyanthracene in polymerization of methyl methacrylate or styrene and considerably different rates of its decomposition in ethyl acetate and in benzene support rather the presumption of significant induced decomposition of this initiator.

The aim of our work was to determine the role of induced decomposition of 9,10-dioxyanthracene in overall decomposition process. On account of it we have measured corresponding decomposition rates in a wide concentration range by means of both the chemiluminescence method for lower concentrations and the calorimetry for higher concentration of peroxide.

Experimental

9,10-Dioxyanthracene was prepared by photooxidation of anthracene in chloroform solution in the presence of methylene blue as photosensitizer [4].

Recrystallized photooxidation product, the purity of which was according to gel permeation chromatography satisfactory, was identified by infrared and ultraviolet spectroscopy [2].

Calorimetric measurements were performed on the differential scanning calorimeter Perkin—Elmer DSC-1B. The samples for measurements of weight from 1 to 10 mg were weighed into aluminium pans which were pressed gastightly altogether with caps. The remained amount of oxygen in the reaction pan was approximately one hundred times less than the amount of peroxide. Prior to thermostating sample to measuring temperature the samples containing naphthalene and peroxide were heated at 82°C for 1 min because of melting of naphthalene and homogenization of peroxide in naphthalene solution.

Chemiluminescence measurements were carried out on spectrometer PU SNK 7M which was made at the Institute of Chemical Physics, Academy of Sciences of USSR, Moscow. Maximum sensitivity of photomultiplier FEU-38 used in spectrometer is at 470 nm. Chemiluminescence intensity was measured in relative units, one relative unit (rel. u.) corresponding to the current 1.8×10^{-13} A at the resistance of circuit 1×10^{11} ohm. Chemiluminescence measurements were carried out in nitrogen atmosphere with the approximate weight of sample 1 g.

The decomposition reaction was investigated by both methods up to 90% of conversion of peroxide.

Results

The rates of released reaction heat were in dependence on peroxide concentration measured at two temperatures.

Reaction half times (Table 1) do not depend on concentration of peroxide in the range of initial peroxide concentrations from 7 to 27% of weight.

For lower concentrations of peroxide the sensitivity of calorimetric method is not sufficient enough to give reliable results. To encompass the range of lower concentrations of peroxide the thermal decomposition of 9,10-dioxyanthracene in solution was followed by chemiluminescence method which is based on the measurement of light emission accompanying decomposition process [5]. We have suggested that the rates of both the reaction heat release and the light emission are determined by the same process, *i.e.* decomposition reaction of peroxide. This assumption is supported by similar values of activation energies

Table 1

Halftimes ($\tau/2$) of decomposition of 9,10-dioxyanthracene in naphthalene at 120 and 130°C and different initial concentrations $[OA]_0$

T °C	$[OA]_0$ weight %	$\tau/2$ s
120	7.5	83
	13.1	86
	16.5	70
	23.0	87
130	5.5	37
	10.3	30
	12.9	32
	27.7	32

determined from rate constants obtained from calorimetric measurements for higher concentrations of peroxides and from chemiluminescence measurements for lower concentrations of peroxide (115 and 118 kJ mol^{-1}, respectively).

Similarly as in calorimetric measurements time course of chemiluminescence intensity exhibits maximum (Fig. 1), which at the first sight may be accounted for only by heating of sample to measuring temperature. About three times longer interval of appearance of maximum on chemiluminescence records when compared to calorimetrical ones corresponds to different weight of samples used in both kinds of measurements as well as to different conditions of heat transfer (aluminium pan and a small amount of sample in calorimetry and glass ampule and more than one hundred times higher amount of sample in chemiluminescence). The other cause of the shift of maximum to shorter times in calorimetry measurements seems to be higher concentration of peroxide in solution. Provided that the temperature increased the similar influence on shortening of time of maximum on observed dependences was noticed. The temperature coefficient of rate at which maximum was reached was in both cases ~125 kJ mol^{-1}.

Maximum on luminescence or calorimetric dependences may be affected also by other factors which were not analyzed experimentally. From the obtained data it ensues that the existence of maximum in the course of investigated curves is determined also by the proper process of decomposition reaction.

Chemiluminescence measurements were evaluated from the postmaximum decreasing parts of the corresponding curve as a reaction of the first order even though the first-order kinetics were fulfilled satisfactory to the intensity decrease from 70 to 90% of maximum value. Above these values there occurs a decrease in the rate of decomposition with regard to the first-order scheme.

This may be a consequence of the fact that the first-order rate constant proves to be dependent on initial concentration of peroxide (Table 2) showing a decrease with the decrease of peroxide concentration.

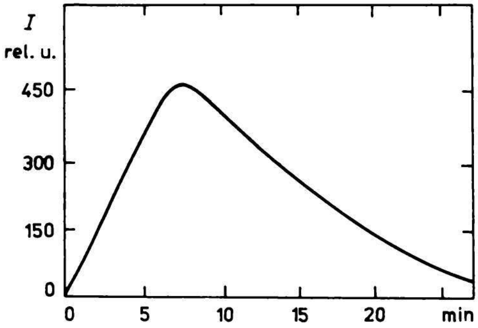

Fig. 1. Course of chemiluminescence intensity for decomposition of 8.2 mg of 9,10-dioxyanthracene soluted in 1 g of naphthalene. Temperature 120°C, nitrogen atmosphere.

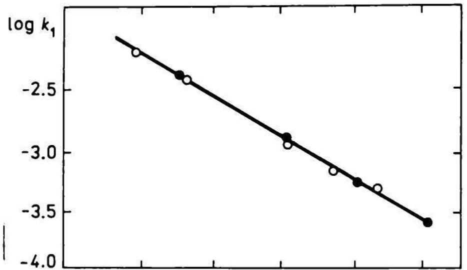

Fig. 2. Dependence of log k_1 on reciprocal value of temperature for decomposition of 9,10-dioxyanthracene in methyl methacrylate (●) and in 2-bromonaphthalene (○). Initial concentrations are 5×10^{-3} mol dm^{-3} for methyl methacrylate and 1×10^{-2} mol dm^{-3} for 2-bromonaphthalene.

Table 2

Apparent rate constants k_1 of the first-order reaction for decomposition of 9,10-dioxyanthracene i naphthalene and methyl methacrylate at 120°C and different initial concentrations

Solvent			
Naphthalene		Methyl methacrylate	
mol dm^{-3}	$10^4\,k_1$, s^{-1}	mol dm^{-3}	$10^4\,k_1$, s^{-1}
0.003	4	0.0007	5
0.020	10	0.0024	10
0.039	17	0.0048	13
0.062	25	0.0095	17

It is worth noticing that under comparable conditions rate constants of decomposition of 9,10-dioxyanthracene in methyl methacrylate are several times higher than those in naphthalene

In the range of lower concentrations of 9,10-dioxyanthracene the temperature dependence of rate constants (Fig. 2) has almost the same activation energy but it has a considerably lower frequency factor than that for decomposition at higher concentrations of peroxide

$$k = 6 \times 10^{12} \exp(-118\,000/RT)\ \mathrm{s}^{-1}$$

Discussion

Before evaluation of the results obtained for decomposition reaction of 9,10-dioxyanthracene one should analyze the reasons of changes of apparent rate constants dependent on initial concentration of 9,10-dioxyanthracene in solvent. Consider that the increase of rate constant of 9,10-dioxyanthracene decomposition is brought about by chain decomposition of peroxide induced by free radicals. The initial rate of decomposition of peroxide described by apparent rate constant k_1 of the first-order reaction and by initial concentration of 9,10-dioxyanthracene $[\mathrm{OA}]_0$ equals the sum of rates of both the spontaneous and induced decomposition, as follows

$$k_1[\mathrm{OA}]_0 = k_s[\mathrm{OA}]_0 + k_i[\mathrm{OA}]_0^n$$

and, after division by $[\mathrm{OA}]_0$

$$k_1 = k_s + k_i[\mathrm{OA}]_0^{n-1}$$

where k_s denotes the rate constant of spontaneous and k_i rate constant of induced decomposition, respectively. Exponent n depends on reactivity and concentration of primary radicals arisen from peroxide as well as on concentration of radicals of reaction medium [3]. As it follows from extrapolation of k_1 values to zero concentration of peroxide $[OA]_0 \rightarrow 0$ (Table 2), k_1 is markedly higher than k_s and, consequently the approximate value of n may be determined from the slope s of linear dependence of $\log k_1$ against $\log [OA]_0$ (Fig. 3) ($s \doteq n-1$ for $k_1 \gg k_s$). Exponent n evaluated in such a way equals approximately 1.5 for chemiluminescence measurements in the range of lower concentrations of peroxide while that for higher concentrations measured by calorimetry is $n \doteq 1$.

Different values of n correspond to different mechanisms of induced decomposition and termination. On the basis of general analysis referred to in [6] the order of chain reaction of induced decomposition equalled one sets in the case when radicals of solvent react with peroxide preferably and termination consists in mutual reaction of both the solvent and decomposing peroxide radicals.

Bringing the concentration of peroxide down under a certain level manifests itself in such a change of mechanism of termination in which only mutual interaction of solvent radicals occurs. Subsequently, the order of induced decomposition and measured apparent rate constant of decomposition reaction depend on

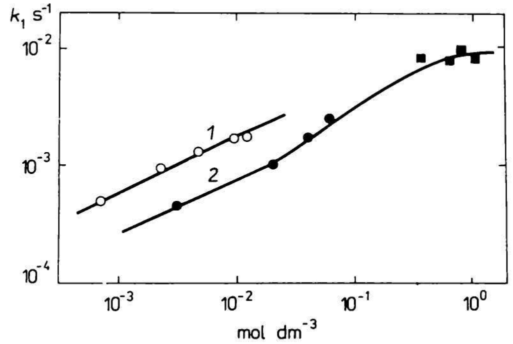

Fig. 3. Logarithmic dependence of overall rate constant of decomposition of 9,10-dioxyanthracene k_1 s^{-1} on concentration of 9,10-dioxyanthracene in methyl methacrylate (*1*) and in naphthalene (*2*) at temperature 120°C. Full squares correspond to calorimetric measurements, the circles and full circles are derived from chemiluminescence measurements.

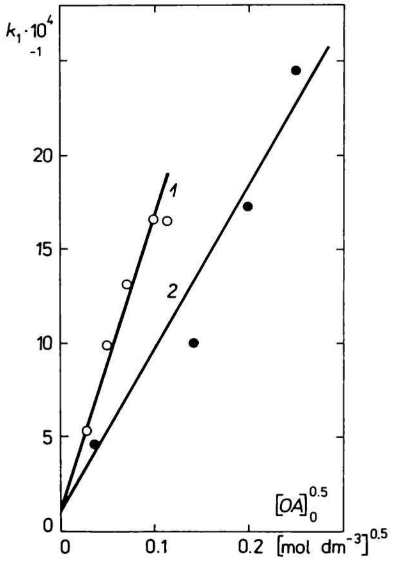

Fig. 4. Determination of rate constants of spontaneous (k_s) and induced decomposition (k_i) from the dependence $k_1 = k_s + k_i [OA]_0^{0.5}$ for methyl methacrylate (*1*) and naphthalene (*2*). Temperature 120°C.

peroxide concentration. Consequently, as if the increase of peroxide concentration led to relative inhibition of induced decomposition.

Extrapolation of apparent rate constants of decomposition of 9,10-dioxyanthracene to zero concentration of peroxide (Fig. 4) yields the same rate constant of spontaneous decomposition for two solvents at 120°C ($\sim 1\times 10^{-4}\ \mathrm{s}^{-1}$).

Complex rate constant of induced decomposition [6] of 9,10-dioxyanthracene in methyl methacrylate is approximately twice higher than that for naphthalene ($k_i = 1.56\times 10^{-2}$ and $0.87\times 10^{-2}\ \mathrm{dm}^{1.5}\ \mathrm{mol}^{-0.5}\ \mathrm{s}^{-1}$) which is likely to correspond to higher reactivity with respect to peroxide of alkyl radicals when compared to aryl radicals. At the same temperature and for 20% of weight of 9,10-dioxyanthracene in naphthalene the overall rate constant is about one hundred times higher than that for spontaneous decomposition. It may be concluded, therefore, that under given conditions, 9,10-dioxyanthracene decomposes by chain mechanism almost exclusively. On the basis of preceding interpretation, kinetics parameters measured for decomposition reaction of 9,10-dioxyanthracene are not, thus, valid for spontaneous but for induced decomposition of different mechanisms. Similarly the equal values of activation energy do not imply, therefore, to spontaneous decomposition, but they ensue from similar activation energies of induced decompositions. Taking into account derived complex constants [3, 6] for induced decomposition of the first order the overall activation energy is given as a function of activation energies of transfer reaction of solvent radicals to 9,10-dioxyanthracene (E_{tS}), primary radicals reaction with solvent (E_{tA}), and termination reaction of solvent radicals with primary radicals (E_{rSA}), respectively

$$E_{tS} + 0.5E_{tA} - 0.5E_{rSA} = 125\ \mathrm{kJ\ mol}^{-1}$$

For the order of induced decomposition equalled 1.5 it holds

$$E_{tS} + 0.5E_{S} - 0.5E_{rSS} = 125\ \mathrm{kJ\ mol}^{-1}$$

where E_S is activation energy of spontaneous decomposition and E_{rSS} is activation energy of recombination of solvent radicals.

Comparing both equations and neglecting the low value of activation energy of termination reactions we obtain

$$E_{tA} \doteq 0.5E_S$$

which is in qualitative agreement with many experimental data for similar reactions investigated so far [7].

The difference in preexponential coefficients may be explained similarly on the basis of different rate constants of induced decomposition of first and three halves orders which are the products and ratios of corresponding rate constants of different elementary reactions of chain process.

Chain mechanism of decomposition of transannular peroxide accounts well also for the great sensitivity of the process to different conditions of reaction in solid state. Small retardation of spontaneous decomposition or deactivation of primary radicals will usually do for elimination of subsequent amplificative stage of decomposition reaction. This fact may be the reason of a relatively great scattering of results as far as the decomposition temperature of 9,10-dioxyanthracene is concerned [8]. In the literature, the following decomposition temperatures are referred to: from 139 to 143°C [4], 146°C [9], 160°C [10], and 166°C [11]. The similar difference in decomposition temperature was observed in our experiments, too, in dependence on whether 9,10-dioxyanthracene was recrystallized from carbon disulfide (decomposition temperature 114°C) or from benzene (139°C). These temperatures were recorded for sample weight 1 mg and at the heating rate 4°C/min.

Data concerning the course of induced decomposition are important particularly from the viewpoint of functioning of 9,10-dioxyanthracene as an initiator of chain reaction. From the great role of induced decomposition one may assume that initiation efficiency of such kind of initiator will be relatively low. The increase of initiation ability of this initiator may be attained in such systems which contain substrate reactive with regard to primary radicals and, at the same time, secondary radicals unreactive towards 9,10-dioxyanthracene.

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