

Initiation of radical reactions by thermal decomposition of alkyl *tert*-butyl monoperoxalates

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Polymerization of methyl methacrylate at 30 °C and oxidation of ethylbenzene at 60 °C initiated by alkyl *tert*-butyl monoperoxalates (alkyl = methyl, isopropyl, *tert*-butyl, *n*-pentyl and *n*-decyl) of known rate constants of monomolecular decomposition have been studied. According to the initial rate, the initiation efficiency of individual peroxalates decreases in the order:

tert-butyl, isopropyl, methyl, *n*-decyl, *n*-pentyl

It was found that the by-products of decomposition — alkyl *tert*-butyl carbonates — also decompose above 60 °C. The rate of decomposition depends on the bulkiness of the alkyl group in the alkyl *tert*-butyl monoperoxalates.

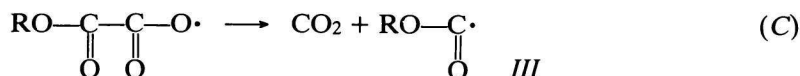
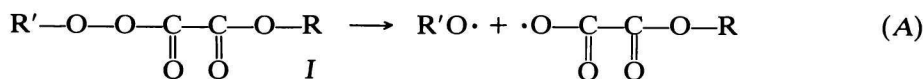
Изучены процессы полимеризации метилметакрилата при 30 °C и окисления этилбензола при 60 °C, инициируемые алкил(*трет*-бутил)монопероксалатами (алкил = метил, изопропил, *трет*-бутил, *n*-пентил и *n*-децил) с известными константами скоростей мономолекулярного разложения. В соответствии с начальной скоростью, эффективность инициирования отдельными пероксалатами уменьшается в ряду:

трет-бутил, изопропил, метил, *n*-децил, *n*-пентил

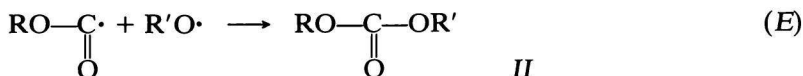
Найдено, что побочные продукты разложения — алкил(*трет*-бутил)-карбонаты — также разлагаются при температурах, высших 60 °C. Скорость разложения зависит от объемности алкил-группы в алкил(*трет*-бутил)монопероксалатах.

Dialkyl monoperoxalates ($R'-O-O-CO-CO-OR$) (*I*) decompose at a measurable rate even at room temperature giving mainly CO_2 [1—5] and some yield of dialkyl carbonates (*II*). As a consequence of reaction of $R'O\cdot$ radicals with the solvent RH there is formed also alcohol $R'OH$.

It is assumed that decomposition of *I* starts at the O—O bond with subsequent fragmentation of oxaloyloxy radicals according to the scheme



The radicals *III* either decarbonylate or terminate



Dependence of decomposition rate on the character of the alkyl group R indicates that in addition to the scheme (A—E) (asynchronous mechanism), decomposition of *I* through a cyclic transition state (synchronous mechanism) should be taken into account. Peroxalates could, like dioxethanes [6—9], give quite a high quantum yield of chemiluminescence. Decomposition of peroxides such as peroxy esters [10], diperoxy oxalates [11, 12], peroxy lactones [13] and others [14] in different solvents is always accompanied by chemiluminescence. This method was also used in our case of the oxidation of ethylbenzene initiated by alkyl *tert*-butyl monoperoxalates. The process was studied with regard to the presence of an activator of chemiluminescence, to the character of the solvent and to the presence of oxygen in the solution. The effect of individual peroxalates on oxidation of ethylbenzene was compared with their efficiency in polymerization of methyl methacrylate.

Experimental

Alkyl *tert*-butyl monoperoxalates and *tert*-butyl carbonates were prepared by the procedure already described [1, 2].

The chemiluminescence measurements were made on a PU SNK 7M spectrometer, produced in the Institute of Chemical Physics, Moscow. The apparatus is equipped with a SbNaKCs photocathode of maximum spectral sensitivity at 460 nm. Solutions of peroxyalate in ethylbenzene or chlorobenzene with 9,10-dibromoanthracene as activator were put into the dark chamber of the apparatus and the variation of chemiluminescence intensity with time was registered during the flow of O₂ or N₂. The chemiluminescence intensity for a given voltage applied to the photomultiplier was expressed in arbitrary units (a.u.). 1 a.u. corresponds to the current 3×10^{-13} A at a resistance of circuit 1×10^{11} ohms.

Methyl methacrylate free of inhibitor was redistilled twice in N₂ before each experiment. The volume of monomer used in polymerization was 4 cm³. The polymerization was carried out in glassy ampoules sealed in nitrogen atmosphere. After some time of reaction the polymer was precipitated with methanol and dried to constant mass.

Results and discussion

In the presence of 9,10-dibromoanthracene as an activator, the intensity of chemiluminescence during oxidation of ethylbenzene at 60 °C, initiated by alkyl *tert*-butyl monoperoxalates (the initial concentration of 1.6×10^{-2} mol dm⁻³) increases from initial low value, goes to a maximum and then decreases (Fig. 1).

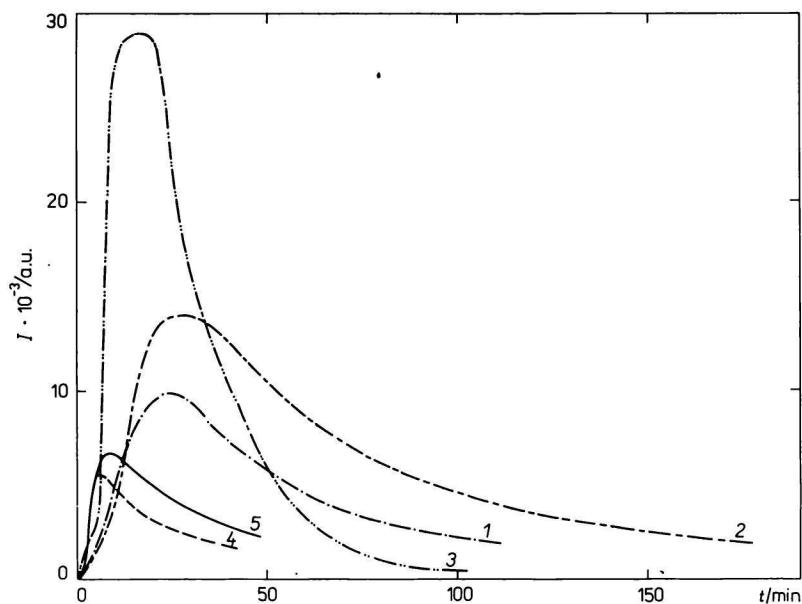


Fig. 1. Courses of chemiluminescence intensity accompanying initiated oxidation of ethylbenzene at 60 °C. Initiators: alkyl (R) *tert*-butyl monoperoxalates.

R: methyl (1), isopropyl (2), *tert*-butyl (3), n-pentyl (4), and n-decyl (5). Initial concentration of peroxyalates: 1.7×10^{-2} mol dm⁻³, concentration of activator (9,10-dibromoanthracene) 1.9×10^{-3} mol dm⁻³.

The initial increase to the maximum corresponds to the sample heating to the measuring temperature; the values of chemiluminescence intensity in maximum I_{\max} are then at a given temperature proportional to the initial rate of oxidation. The presence of chemiluminescence activator leads to some additional kinetics problems. There always exists e.g. possibility of quenching of excited states of activator which are populated by energy transfer from the excited acetophenone [15]. To overcome this, we have considered the following sequence of elementary reaction steps for the description of decreasing parts of chemiluminescence intensity vs. time courses.

In the presence of oxygen, all primary radicals of initiator (monoperoxalate) are after their reaction with ethylbenzene transformed to ethylbenzene peroxy radicals. Their recombination gives acetophenone in its excited triplet state X^* [15]. Then there follows the transfer of energy to the 9,10-dibromoanthracene A and the quenching of A^* particles by initiator I or by products P of its decomposition



In the scheme (F—J) v denotes the rate of initiation, and k_{XA} , k_{AI} , k_{AP} , and k_{chem} are individual rate constants.

Chemiluminescence intensity is determined by the rate of step (J), i.e. by the relation

$$I_{\text{chem}} = k_{\text{chem}}[A^*] \quad (1)$$

The steady state concentration of the excited molecules can be determined from the equation

$$v = k_{AI}[A^*][I] + k_{AP}[A^*][P] + k_{\text{chem}}[A^*] \quad (2)$$

Substituting the value of $[A^*]$ from eqn (2) to eqn (1) we have

$$I_{\text{chem}} = \frac{k_{\text{chem}} \cdot v}{k_{AI}[I] + k_{AP}[P] + k_{\text{chem}}} \quad (3)$$

Since the alkyl monoperoxalate decomposes by a first-order process, the values of concentrations I, P and the rate of initiation v can be expressed as the following functions of time

$$v = k_i[I]_0 e^{-kt}, [I] = [I]_0 e^{-kt}, [P] = [I]_0 \cdot (1 - e^{-kt}) \quad (4)$$

where k_i is the rate constant for initiation of the oxidation, $[I]_0$ is the initial concentration of the initiator, and k is the rate constant of its decomposition.

After further substitution of eqn (4) into eqn (3), we thus finally receive the equation

$$I_{\text{chem}} = \frac{a \cdot e^{-kt}}{1 + b \cdot e^{-kt}} \quad (5)$$

in which constants a and b are complex expressions of the corresponding constants such as

$$a = \frac{k_{\text{chem}} \cdot k_i [I]_0}{k_{\text{chem}} + [I]_0 k_{\text{AP}}} \quad (6)$$

$$b = \frac{[I]_0 \cdot (k_{\text{AI}} - k_{\text{AP}})}{k_{\text{chem}} + [I]_0 \cdot k_{\text{AP}}} \quad (7)$$

The values of parameters a , b , and k of eqn (5), estimated by the optimization of the decreasing sections of chemiluminescence intensity vs. time curves are given in Table 1. The highest rate constant k of decomposition of alkyl *tert*-butyl

Table 1

Rate constants k' of alkyl *tert*-butyl monoperoxalates decomposition (data from the previous papers [1, 2]) and parameters k , a , and b of eqn (5), determined from chemiluminescence curves for oxidation of ethylbenzene in O_2 at $\theta = 60^\circ C$

R	Ethylbenzene $\frac{k' \cdot 10^5}{s^{-1}}$	Benzene $\frac{k' \cdot 10^5}{s^{-1}}$	Ethylbenzene $\frac{k \cdot 10^5}{s^{-1}}$	$\frac{a}{\text{a.u.}}$	$\frac{b}{\text{a.u.}}$
Methyl	35.0	24.5	30.0	11.073	-0.558
Isopropyl	48.6	45.6	25.0	17 793	-0.423
<i>tert</i> -Butyl	63.0*	249.0**	98.3	120 627	1.051
n-Pentyl	28.9	25.2	3.3	1 856	-0.983
n-Decyl	28.8	39.9	33.3	4 777	-0.519

* The value for $45^\circ C$, Ref. [3–5]; **the value for $55^\circ C$, Ref. [3–5].

monoperoxalates in ethylbenzene was found for alkyl = *tert*-butyl. The positive values of b indicate that according to the above analysis, alkyl *tert*-butyl monoperoxalate itself is an efficient quencher of the excited states of 9,10-dibromoanthracene. This is valid in our case only for *ditert*-butyl monoperoxalate; all the others quench more likely by the products of their decomposition ($b < 0$).

The values of rate constants k of decomposition of peroxalates for alkyl = methyl, isopropyl, *n*-decyl are comparable with those found in the paper [1, 2]; only for alkyl = *n*-pentyl we have obtained a lower value.

It is of interest that the courses of chemiluminescence intensities measured in nitrogen atmosphere in chlorobenzene show no dependence of maximum intensity I_{\max} either on type of decomposing initiator (Fig. 2) or on the temperature (Table 2). The intensities are very low. It seems, therefore, that the synchronous

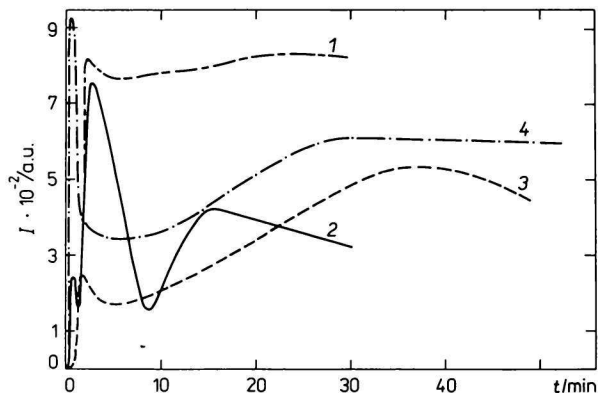


Fig. 2. Time courses of chemiluminescence intensity for alkyl (R) *tert*-butyl monoperoxalates decomposition in chlorobenzene in an inert atmosphere (N_2). The initial concentration of peroxalates was $1.7 \times 10^{-2} \text{ mol dm}^{-3}$.

R: methyl (1), *tert*-butyl (2), *n*-pentyl (3), and *n*-decyl (4). Temperature: 70°C , without activator.

Table 2

Temperature dependence of the numerical values of maximal chemiluminescence intensity I_{\max} in a.u. for decomposition of alkyl *tert*-butyl monoperoxalates in chlorobenzene

Alkyl	50.8°C	60.0°C	70.0°C
Methyl	735	900	820
Isopropyl	460	720	—
<i>tert</i> -Butyl	685	830	760
<i>n</i> -Pentyl	350	320	245
<i>n</i> -Decyl	1075	1125	980

mechanism of the peroxalate decomposition is of minor significance. The chemiluminescence observed in the presence of N_2 will probably be due to the traces of oxygen in solution or adsorbed on the walls of the reaction vessel. At higher temperatures ($70\text{ }^\circ\text{C}$), however, a second maximum appears on the intensity vs. time course observed in nitrogen. After this second maximum, the chemiluminescence intensity slowly decreases.

Asynchronous decomposition of alkyl *tert*-butyl monoperoxalates with an easy escape of free radicals from the reactions cage is a reason why these compounds are initiators of the radical polymerization. Conversion curves of methyl methacrylate polymerization initiated by alkyl *tert*-butyl peroxalates at $c = 1 \times 10^{-2}\text{ mol dm}^{-3}$ show that polymerization takes place even at the laboratory temperature (Fig. 3).

The initiation efficiencies corresponding to the values of rate constants of peroxalate decomposition decrease in the sequence of alkyl

tert-butyl, isopropyl, methyl, *n*-decyl, *n*-pentyl

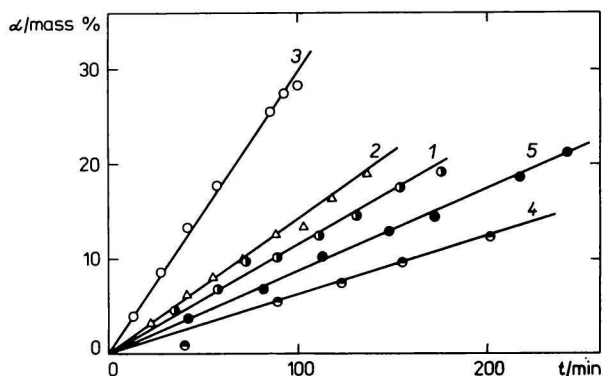


Fig. 3. Conversion curves of methyl methacrylate polymerization initiated by alkyl (R) *tert*-butyl monoperoxalates ($c_0 = 1 \times 10^{-2}\text{ mol dm}^{-3}$) at $30\text{ }^\circ\text{C}$.

R: methyl (1), isopropyl (2), *tert*-butyl (3), *n*-pentyl (4), and *n*-decyl (5).

From the concentration dependence of the initial polymerization rate for alkyl *tert*-butyl monoperoxalates where alkyl is *tert*-butyl and methyl (Table 3) it may be found that the reaction order with respect to the initiator is 0.5.

The second maximum on the chemiluminescence intensity vs. time curves at temperatures above $70\text{ }^\circ\text{C}$ leads to the idea that the radical reactions are initiated not only by monoperoxalate, but also by some of the products of its decomposition. For this purpose the alkyl *tert*-butyl carbonates were synthesized and tried as the initiators of methyl methacrylate polymerization at $60\text{ }^\circ\text{C}$; (initial concentration $5 \times 10^{-2}\text{ mol dm}^{-3}$) (Table 4).

Table 3

The initial rates v_0 and the orders n estimated according to the expression $v_0 = k \cdot c_0^n$ of methyl methacrylate polymerization initiated by alkyl *tert*-butyl monoperoxalates at 30 °C
 c_0 is the initial concentration of initiator and k is proportionality constant

Alkyl	$\frac{c_0 \cdot 10^3}{\text{mol dm}^{-3}}$	$\frac{v \cdot 10^6}{\text{mol kg}^{-1} \text{ s}^{-1}}$	n
Methyl	1	0.67	0.47
	5	1.42	
	10	1.92	
	50	4.25	
Isopropyl	10	2.37	
<i>tert</i> -Butyl	1	1.25	0.56
	5	3.17	
	10	5.07	
	50	10.83	
n-Pentyl	10	1.03	
n-Decyl	10	1.47	

Table 4

Polymerization of methyl methacrylate initiated by alkyl *tert*-butyl carbonates at 60 °C

Alkyl	Conversion of monomer to polymer after 240 min/mass %
Ethyl	14.5
Isopropyl	5.3
n-Decyl	1.5
Thermal polymerization of methyl methacrylate	1.0

It was really found that alkyl *tert*-butyl carbonates are able to initiate polymerization. This proceeds, of course, more slowly, than it was in the case of corresponding alkyl *tert*-butyl monoperoxalates, but cannot be neglected. Especially the effect of carbonates with smaller alkyls such as ethyl or isopropyl is significant. Low yield of the carbonates found after decomposition of alkyl

tert-butyl monoperoxalates in ethylbenzene at 60 °C seems to correspond to their subsequent participation in the initiation reaction.

According to the previous data [1, 2] the yields of alkyl *tert*-butyl carbonates per mole of decomposed alkyl *tert*-butyl monoperoxalate increase in the order methyl (0.03), ethyl (0.19), isopropyl (0.21), *tert*-butyl (0.23), *n*-decyl (0.32), and *n*-pentyl (0.36).

According to this sequence it may be seen that less stable are the carbonates with smaller alkyls.

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