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INHIBITED OXIDATION OF CUMENE AND POLYMERIZATION OF STYRENE INVESTIGATED BY SOLUTION MICROCALORIMETRY

A. Velikov[1], *L. Matisová-Rychlá*[2*], *R. Broska*[2] *and J. Rychly*[2]

[1]Institute of Crude Oil Chemistry, Academy of Sciences, 634 36 Tomsk, Russia
[2]Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava, Slovak Republic

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Abstract

The application of solution microcalorimetry was demonstrated on two model examples – inhibited oxidation of cumene and radical polymerization of styrene.

From the experimental dependences of the rate of heat release on time, the rate constants k_7 of the interaction of an inhibitor with radicals of substrate ($RO_2^{\cdot}$ or $R^{\cdot}$) in oxidation or in polymerization were determined for the set of inhibitors of N-aryl N-(2-quinone) amine series. It was shown that these compounds are weak inhibitors of oxidation of cumene and rather efficient inhibitor of polymerization of styrene.

Keywords: cumene, oxidation, polymerization, quinone-amine inhibitors, solution microcalorimetry, styrene

Introduction

Efficiency of inhibitors of polymerization of monomers and of oxidation of polymer materials and low molecular hydrocarbons may be tested by monitoring some elementary step of the free radical chain process involved either in initiation, propagation or termination stage of the reaction, which is affected by the presence of an inhibitor. Thus, DSC [1–4], thermogravimetry [5], ESR spectroscopy [6], chemiluminescence [7–16], oxygen absorption [17–20] and spectroscopy methods [21–23] for determination of reaction products can be used, the efficiency of the inhibitor is usually estimated from the inhibition period of oxidation. From this viewpoint, until now little attention has been paid to the solution microcalorimetry where the rate of the heat released (Q) in the propagation stage of the reaction prevails the heat effects from other elementary reactions and thus it is directly proportional to the rate of oxidation or polymerization:

$$Q = \Delta HVw \tag{1}$$

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[*] Author to whom all correspondence should be addressed.

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where, ΔH is the reaction enthalpy, V is the volume of the reaction system and w is the rate of the reaction.

The method appears particularly suitable for investigation of the course of the inhibited chain radical reactions in oxidation of polymers and low molecular hydrocarbons [24] taking place in solutions. The oxidation of low molecular hydrocarbons like ethyl benzene, cumene and edible oils are the most representative examples.

In the present paper, the oxidation of cumene and polymerization of styrene initiated by 2,2-azobis(isobutyronitril)(AIBN), inhibited by the set of N-aryl N-2-(1,4-quinone) amines has been examined at 60°C using the Privalov's solution microcalorimeter. The inhibition pattern of the respective additive was investigated with the aim to determine the rate constant of transfer reaction of the chain propagating radicals to the inhibitor.

Experimental

Procedure

The rate of the heat release during inhibited oxidation of cumene and/or polymerization of styrene was measured by the calorimeter MKDP-2 produced at the Institute of Crude Oil Chemistry, Tomsk, Russia.

The solution of an inhibitor in the hydrocarbon (cumene and styrene) (4 ml) were introduced to the teflon reaction vessel of the overall volume 10 ml. Initiator was placed into the special open capsule floating on the surface of the liquid.

In oxidation studies, the solution has been bubbled through by oxygen and the reaction vessel was gas-tightly closed. In polymerization experiments, a special reaction vessel has been used enabling the degassing the system from oxygen in a repeated cycle of freezing and filling with nitrogen. The reaction vessel was placed in the measuring head of the calorimeter. When the system of reactants was thermostated to a given temperature the semirotating motion of calorimetric head provided the mixing and dissolution of initiator in the solution. The motion of the head was kept throughout the measurements.

Chemicals

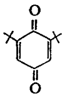
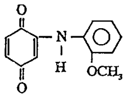
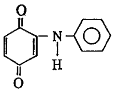
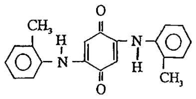
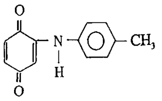
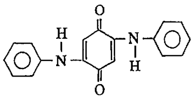
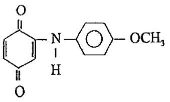
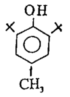
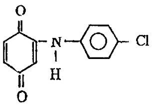
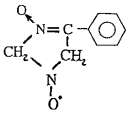
AIBN was used as the initiator of polymerization of styrene and oxidation of cumene. It was purified by two-fold recrystallization from ethanol.

Cumene was purified by extraction with concentrated H_2SO_4, with solution of NaOH, water and dried over Na_2CO_3, vacuum distilled and filtered through a column filled with activated Al_2O_3.

Styrene was purified with 5% water solution of NaOH, washed with water, dried over Na_2CO_3 and vacuum distilled.

Structure of inhibitors used in both the oxidation and polymerization measurements is given in the Table 1. Substances 2–8 were synthesized and kindly supplied by the group of Schulz from the University Merseburg, Germany. Besides the compound 1 they all contain several reactive sites in one molecule. Benzoquinone moi-

Table 1 Stucture of the inhibitors studied

1		6	
2		7	
3		8	
4		9	
5		10	

ety of the inhibitor was assumed to provide an inhibiting effect in radical polymerization of vinyl monomers reacting with the growing alkyl radicals. Aromatic amine site of a molecule, on the other hand, reacts preferentially with peroxy radicals being formed in oxygen containing atmosphere during oxidation. Substituents on the phenyl ring (compounds 3, 4, 5, 6) performing electron donor ($-CH_3$, $-OCH_3$), or electron acceptor ($-Cl$) effects as well as the unsubstituted compounds composed of one benzoquinone and two amine moieties (compounds 7 and 8) were expected to modify antioxidative efficiency of the inhibitors studied.

Results and discussion

Illustrative plots of the rate of heat release on time for both the oxidation of cumene and polymerization of styrene at 60°C are given in the Figs 1 and 2.

Some important statements follow from the experimental runs:

Dissolution of the initiator after the mixing of reactants is endothermic process. However, the line observed is retained on the endothermic side even in further stages of the process for both the inhibited oxidation and polymerization. Such effect of inhibitors, which appears to be quite typical for quinone amines, was not observed for phenols and aromatic amines. As it was reported in [24] and [25] these compounds gave the line which turned immediately to the exothermic side of the scale when initiator has been dissolved (e.g. the line 9 of Fig. 1 for 2,6-*ditert*-butyl 4-methyl phenol).

For inhibited polymerization of styrene, the dependence of the value of this negative heat effect on the rate of initiation as well as on inhibitor concentration was followed. The plots of the maximum negative values of the heat release on the rate of

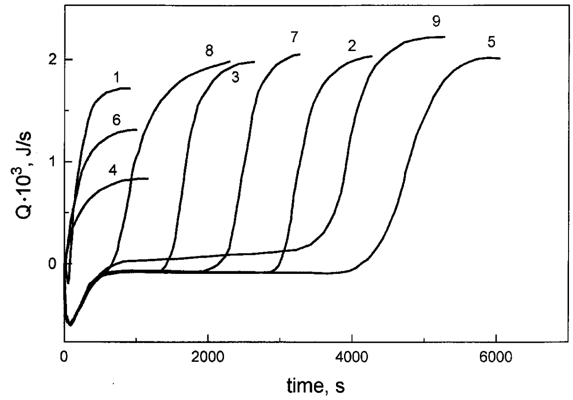


Fig. 1 The plot of the rate of heat release Q *vs*. time t in oxidation of cumene inhibited by substances 1–9 from the Table 1. Initiator: AIBN; T=60°C; [InH]=$2.5\cdot10^{-4}$ mol l^{-1}; The rate of initiation $w_i=3.4\cdot10^{-8}$ mol l^{-1}s^{-1}, w_i were calculated according to the relation $w_i=ek$[AIBN] where $k=1.58\cdot10^{15}\exp(-30800/RT)$; Line 9 shows the effect of 2,6-*ditert*-butyl-4-methyl-phenol (ionol); its initial concentration $7\cdot10^{-5}$ mol l^{-1}

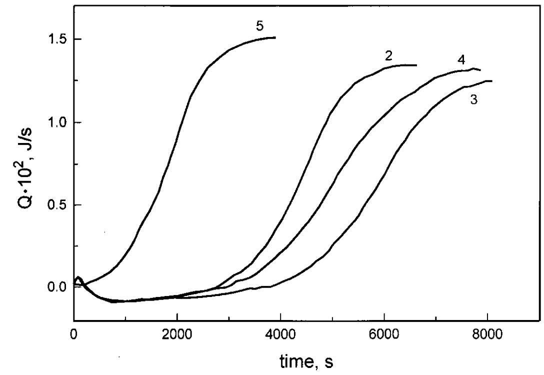


Fig. 2 The plot of the heat release *vs*. time in the polymerization of styrene in the presence of inhibitors 2, 3, 4 and 5 from Table 1 at 60°C. Initiator: AIBN; [InH]=$7.5\cdot10^{-4}$ mol l^{-1}, $w_i=1.2\cdot10^{-7}$ mol l^{-1}s^{-1}

initiation and initial concentration of inhibitors for the compounds 1 and 10 are shown in the Figs 3 and 4. The main process taking place during the inhibition period appears to be the reaction of growing macroradicals with the molecule of inhibitor. Since with the increase of the rate of initiation the stationary concentration of radicals $R^{\cdot}$ increases too, this might explain the observed linearity between the negative values of the heat released (positive values of heat absorbed) and the rate of initiation. The increase of the negative value of the rate of heat release was observed also for the increase of the initial concentration of inhibitor added (Fig. 4), however, the curve declines from the linearity above the initial concentration of inhibitor: [InH]>$7.5\cdot10^{-4}$ mol l^{-1}. This is explained by decreasing solubility of an inhibitor at its higher initial concentration.

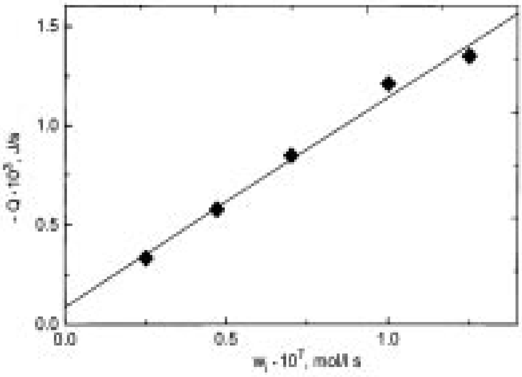


Fig. 3 The plot of the maximum rate of negative heat release in the inhibition period of polymerization of styrene *vs*. the rate of initiation. Initiator: AIBN; [InH] (Compound 1 from Table 1)=$1\cdot10^{-3}$ mol l^{-1}; T=60°C

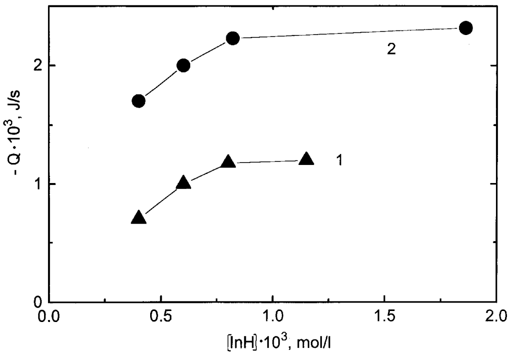


Fig. 4 The plot of the maximum rate of negative heat release in the inhibition period of polymerization of styrene *vs*. concentration of inhibitors. Initiator: AIBN; $w_i=1.2\cdot10^{-7}$ mol $l^{-1}s^{-1}$; T=60°C; Line 1: InH 1; Line 2: InH 10

Experimental studies presented in Figs 1 and 2 thus provide an evidence of the endothermicity of the interaction of $R^{\cdot}$ and $RO_2^{\cdot}$ radicals with the set of inhibitors (the compounds 2–8, 10 in Table 1).

There are not available literature data on ΔH values describing the interactions of peroxy radicals with compounds of Table 1. Handbook of Antioxidants [26], brings the data of ΔH for the interaction of *tert*-$RO_2^{\cdot}$ with 4-NO_2 substituted diphenyl amine which is 14.3 kJ mol^{-1} while that for *sec*-$RO_2^{\cdot}$ it is 7.4 kJ mol^{-1}. One can suppose, that the endothermicity in a similar extent is valid also for the interaction of cumene peroxy radical with inhibitors 2–8, 10 of Table 1.

We have neglected the heat effects due to the initiation and termination reactions. Such an assumption is justified by the following calculations:

The rate of the heat release Q_i due to the initiation reaction should be:

$$Q_i = \Delta H_{init} V w_i \tag{2}$$

The rate of initiation in polymerization of styrene at 60°C is w_i= $1.2{\cdot}10^{-7}$ mol $l^{-1}s^{-1}$ (calculated from the amount of initiator used, the rate constant of initiator decomposition and yield of radicals from the cage 0.8 [27]), the reaction volume V=$4{\cdot}10^{-3}$ l and the heat of reaction ΔH_{init} from [28] is 131 kJ mol^{-1}. Accordingly, the rate of the heat release calculated from these values should be $6.28{\cdot}10^{-5}$J s^{-1}. Comparing it with the value of the heat release measured under the stationary conditions of polymerization of styrene (Q_{stat}=$1.5{\cdot}10^{-2}$ J s^{-1}), Q_i takes only 0.5% of Q_{stat}. For oxidation of cumene Q_i=$1.78{\cdot}10^{-5}$ J s^{-1}, which is again lower than 1% of Q_{stat} (Figs 1 and 2).

The contribution of recombination reactions of alkyl or alkylperoxy radicals to the overall reaction heat can be estimated for the steady course of the reaction in which the rate of initiation equals to the rate of termination. The exothermicity of the thermination reaction is about 400 kJ mol^{-1} for thermination of $RO_2^{\cdot}$ radicals [29] and 270–340 kJ mol^{-1} for termination of alkyl radicals. In the oxidation or polymerization experiments, the only termination reaction is the reaction of either two peroxy radicals or the reaction of two growing polymerization alkyl radicals. The correction on the heat released in termination reactions can thus reach 3% of the stationary value of the heat measured in oxidation [24] and may be neglected, too.

In the first characterization of the inhibition efficiency, the induction period usually shows how long time a certain inhibitor withstands the attack of reactive free radicals and converts them to less reactive radicals.

As it is seen from the Figs 1 and 2 the inhibition period depends significantly on the character of substituted groups on the phenyl ring as well as on the initial concentration of inhibitors (Fig. 5). The plot of inhibition period *vs.* the initial concentration of inhibitor is essentially linear.

In oxidation of cumene, the most efficient inhibitor is compound 5 containing –Cl in the position 4 on phenyl ring of N–aryl N-(2-benzoquinone) amine. Ionol (compound 9) is slightly less efficient, followed by the compound 2 having nonsubstituted phenyl ring and 7 which is 2,5-benzoquinone bis/N-(2-toluyl) diamine.

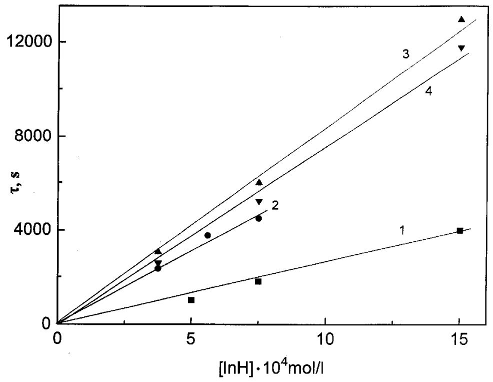


Fig. 5 The plot of inhibition times τ for polymerization of styrene at 60°C *vs.* initial concentration of inhibitors 1–4 from Table 1. The rate of initiation w_i=$1.2{\cdot}10^{-7}$ l $mol^{-1}s^{-1}$

Some efficiency is provided also by compound 3 and 8, which are nonsubstituted N-(2-benzoquinone) N–phenyl amine and corresponding benzoquinone diamine. It is of interest that substitution by methoxy group of phenyl ring either in position 2 or 4 leads practically to the total suppression of inhibition efficiency of benzoquinone amines. The inhibiting efficiency of 2,6-*ditert*-butyl benzoquinone in oxidation of cumene is also very weak. As it is evidenced by the lower value of Q_{stat}, the latter compounds act as retardants of oxidation.

In polymerization of styrene, the most efficient inhibitor appears to be compound 3 (benzoquinone aryl amine substituted by methyl group in position 4 on the phenyl ring), very efficient is also the substitution by methoxyl group in the position 4 on the phenyl ring (compound 4) and nonsubstituted benzoquinone aryl amine (compound 2). On the other hand, the substitution of the phenyl ring by chlorine provides only moderate efficiency in inhibition of polymerization of styrene.

The –Cl substitution on the phenyl ring of the inhibitor (compound 5 in Table 1) thus acts in an opposite way to $-CH_3$ substitution (compound 6) when oxidation of cumene and polymerization of styrene are compared. Inhibitor with chlorine atoms gives the higher inhibition period in oxidation of cumene when compared to $-CH_3$ substitution while in polymerization of styrene it is vice versa. According to [27], however, the reactivity of benzoquinone itself towards alkyl radicals during the polymerization decreases with increasing number of methyl groups in the molecule while the chlorine substitution leads to an increase of the quinone reactivity towards alkyl radicals. This discrepancy indicates that the primary attack of either peroxy radicals during oxidation or alkyl radicals during polymerization is preferably focused on amine group of respective quinone amine.

Inhibition time τ is usually expressed as:

$$\tau = \frac{[\mathrm{InH}]}{w_i} \tag{3}$$

where [InH] is molar concentration of an inhibitor and w_i is the rate of initiation. In the case of AIBN initiation $w_i=2k_d[\mathrm{AIBN}]e$, where k_d is the rate constant of AIBN decomposition, [AIBN] is molar concentration of AIBN and $e=0.8$ is the yield of radicals from the cage.

Induction times τ obtained from the intersections of the straight line of the maximum slope passing through the inflection point and the base line of the time axis (Figs 1 and 2, Tables 2 and 3), however, do not follow exactly the above equation; the effective concentration of inhibitor corresponds very rarely to that calculated from the weighed amount of inhibitor InH. Its effective concentration $[\mathrm{InH}]_{eff}$ can be approximated by the expression:

$$[\mathrm{InH}]_{eff} = fn[\mathrm{InH}], \tag{4}$$

where f is the number of inhibiting functions in one molecule of inhibitor and n is the number of reactive free radicals which can disappear due to one inhibiting function.

Table 2 Experimentally determined and calculated parameters of initiated oxidation of cumene inhibited by inhibitors from the Table 1.
Concentration of inhibitor [InH]=$2.5\cdot10^{-4}$ mol l^{-1} (compounds 1–8); [InH]=$7\cdot10^{-5}$ mol l^{-1} (compound 9), the rate of initiation $w_i=3.4\cdot10^{-8}$ $mol^{-1}s^{-1}$

Comp. No.	$Q_{stat}\cdot10^3$/ J s^{-1}	τ/ s	$k_7/(fn)\cdot10^{-3}$/mol^{-1} s^{-1}		*fn*		$k_7\cdot10^{-4}$/mol^{-1} s^{-1}
			α	β	a	b	α, b
1	1.75	83	7.7	18.5	–	0.03	0.023
2	2.10	3011	14.4	12.5	0.41	0.45	0.65
3	2.00	1476	12.8	13.0	0.20	0.24	0.31
4	0.85	23	2.9	–	–	0.03	0.009
5	2.05	4234	10.3	11.5	0.58	0.67	0.69
6	1.35	23	4.2	15.5	–	0.03	0.012
7	2.10	2276	12.7	11.4	0.31	0.34	0.39
8	2.00	726	9.2	6.8	0.10	0.14	0.13
9	2.25	3633	8.8	7.6	1.76	1.82	1.60[c)]

a – calculated from induction time, presumed initiation rate and concentration of inhibitor [InH] according to Eqs (3) and (4)

b – calculated by non-linear regression analysis of observed curves comparing w_i and w_{eff} determined by fitting of theoretical curves to the experimental runs

c – value k_7 from the previous paper is $2.2\cdot10^4$ l $mol^{-1}s^{-1}$ [32]

α – determined by Bagdassaryan-Bamford method [30]

β – determined by non-linear regression analysis

Table 3 Parameters of polymerization of styrene inhibited by quinone amines from the Table 1. The concentration of inhibitor [InH]=$7.5\cdot10^{-4}$ mol l^{-1}, the rate of initiation w_i= 1.2 10^{-7} $mol^{-1}s^{-1}$

Comp. No.	$Q_{stat}\cdot10^3$/ J s^{-1}	τ/ s	$k_7/(fn)\cdot10^{-3}$/mol^{-1} s^{-1}		*fn*		$k_7\cdot10^{-4}$/mol^{-1} s^{-1}
			α	β	a	b	α, b
2	14.0	3600	79.0	97.0	0.58	0.75	5.90
3	12.8	4700	67.0	102.0	0.78	0.98	6.56
4	14.0	3750	64.0	87.0	0.60	0.85	5.44
5	15.5	1000	53.0	114.0	0.16	0.32	1.70

a – calculated from induction time, presumed initiation rate and concentration of inhibitor [InH] according to Eqs (3) and (4)

b – calculated by non-linear regression analysis of observed curves comparing w_i and w_{eff} determined by fitting of theoretical curves to the experimental runs

α – determined by Bagdassaryan-Bamford method [30]

β – determined by non-linear regression analysis

For example, one radical can react with amino group in transfer reaction giving a more stable $N^{\cdot}$ radical and the second one with this N radical in termination process.

The factors *fn* determined from the induction times and from the known rate of initiation are listed in the Tables 2 and 3 for both oxidation and polymerization experiment.

Methods of evaluation of curves obtained and determination of the rate constant of the transfer of radicals to inhibitor

The rate w of the two qualitatively different processes – thermooxidation and radical polymerization – measured by the solution calorimeter can be characterized formally by the identical equations:

$$w = \mathrm{k}[\mathrm{RH}][\mathrm{P}^{\cdot}] \tag{5}$$

where k is the rate constant of the propagation step, [RH] is the concentration of the substrate and $[\mathrm{P}^{\cdot}]$ denotes the concentration of propagating free radicals (peroxy radicals $\mathrm{RO}_2^{\cdot}$ in oxidation or $\mathrm{R}^{\cdot}$ growth polymerization radicals in polymerization).

Initiated oxidation of hydrocarbons in the presence of an inhibitor InH was described by the classical scheme:

$\mathrm{I}_2 \rightarrow 2\mathrm{I}^{\cdot}$	k_d	
$\mathrm{I}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{IO}_2^{\cdot}$	$\mathrm{k_a}$	
$\mathrm{IO}_2^{\cdot} + \mathrm{RH} \rightarrow \mathrm{IOOH} + \mathrm{R}^{\cdot}$	k_o	0
$\mathrm{R}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{RO}_2^{\cdot}$	k_1	I
$\mathrm{RO}_2^{\cdot} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\cdot}$	k_2	II
$\mathrm{RO}_2^{\cdot} + \mathrm{RO}_2^{\cdot} \rightarrow \text{products}$	k_6	III
$\mathrm{InH} + \mathrm{RO}_2^{\cdot} \rightarrow \mathrm{ROOH} + \mathrm{In}^{\cdot}$	k_7	IV

Here, $\mathrm{I}^{\cdot}$ is the radical derived from initiator, RH is the hydrocarbon substrate, $\mathrm{R}^{\cdot}$ and $\mathrm{RO}_2^{\cdot}$ are alkyl and alkyl peroxy radicals, InH is inhibitor. As the reaction temperature was rather low, the thermal decomposition of hydroperoxides IOOH and ROOH does not contribute to the initiation reaction significantly.

First elementary reaction of radical polymerization is the addition of initiating radical to monomer molecule (M)

$\mathrm{I}^{\cdot} + \mathrm{M} \rightarrow \mathrm{IM}^{\cdot}(\mathrm{R}^{\cdot})$ k_a

The elementary reactions in polymerization are formally identical with those of the above oxidation scheme I–IV; $\mathrm{RO}_2^{\cdot}$ radicals are replaced by $\mathrm{RM}^{\cdot}$ ($\mathrm{R}^{\cdot}$) radicals and instead of transfer reactions II and IV the addition reaction $\mathrm{R}^{\cdot}+\mathrm{M}\rightarrow\mathrm{R}^{\cdot}$ and transfer reaction $\mathrm{InH}+\mathrm{R}^{\cdot}\rightarrow\mathrm{In}^{\cdot}+\mathrm{RH}$ take place.

In both cases of oxidation and polymerization, the presence of inhibitor leads to more or less efficient elimination of the propagation step depending on the value of the ratio $k_7[\mathrm{InH}]/k_2[\mathrm{RH}]$ or $k_7'[\mathrm{InH}]/k_2'[\mathrm{M}]$ (k_2' and k_7' are the rate constants of addition of growing polymerization radicals to monomer and transfer reaction to inhibitor, respectively), which determines the efficiency of the inhibitor. This is why the kinetic course of the process shows a rather distinct inhibition period. During this period, the inhibitor is steadily consumed and the rate of the process ultimately reaches the value as in its absence. The rate of the heat release on time performs thus typical sigmoidal shape.

Stationary conditions for inhibited oxidation and polymerization can be formally described by the identical equations:

$$w_\mathrm{i} = k_6[\mathrm{RO}_2^{\cdot}]^2 + k_7[\mathrm{RO}_2^{\cdot}]\,[\mathrm{InH}] \tag{6}$$

$$w_\mathrm{i} = k_6[\mathrm{R}^{\cdot}]^2 + k_7[\mathrm{R}^{\cdot}][\mathrm{InH}] \tag{7}$$

where w_i is the initiation rate, k_6 and k_7 are the rate constants of termination and reaction of peroxyl or alkyl radicals with an inhibitor.

When the inhibition period ends, the concentration of the inhibitor can be considered as zero. The Eqs (6) and (7) then have the form:

$$w_\mathrm{i} = k_6[\mathrm{RO}_{2\mathrm{stat}}^{\cdot}]^2 \tag{8}$$

$$w_\mathrm{i} = k_6[\mathrm{R}_\mathrm{stat}^{\cdot}]^2 \tag{9}$$

where $[\mathrm{RO}_{2\mathrm{stat}}^{\cdot}]$ and $[\mathrm{R}_\mathrm{stat}^{\cdot}]$ are stationary concentrations of peroxyl and alkyl radicals. Substitution the Eqs (8) and (9) into Eqs (5) and (1) leads to the equations for the rate of the heat release when inhibitor InH has been consumed:

$$Q_\mathrm{stat} = \frac{\Delta H V k_2[\mathrm{RH}]w_\mathrm{i}^{1/2}}{k_6^{1/2}} \tag{10}$$

$$Q_\mathrm{stat} = \frac{\Delta H V k_2[\mathrm{M}]w_\mathrm{i}^{1/2}}{k_6^{1/2}} \tag{11}$$

Substitution of the concentration of peroxy $\mathrm{RO}_2^{\cdot}$ or alkyl $\mathrm{R}^{\cdot}$ radicals expressed from the Eqs (6) and (7), i.e.

$$[\mathrm{RO}_2^{\cdot}] = \frac{-k_7[\mathrm{InH}] + \sqrt{k_7^2[\mathrm{InH}]^2 + 4w_\mathrm{i}k_6}}{2k_6} \tag{12}$$

into Eq. (13),

$$Q_\mathrm{t} = \Delta H V k_2[\mathrm{RH}][\mathrm{RO}_2^{\cdot}] \tag{13}$$

describes the rate of heat release in time *t*.

Two approaches for the estimation of kinetic parameter k_7 of inhibitors were used:

a) Non-linear regression analysis, minimizing the sum of squares for experimental and theoretical courses. The latter were described by the function (13), using the expression (12) for which the concentration of inhibitor was found by parallel solution of the differential Eq. (14) in each iteration step.

$$\frac{\mathrm{d}[\mathrm{InH}]}{\mathrm{d}t} = k_7[\mathrm{RO}_2^{\cdot}]\,[\mathrm{InH}] \tag{14}$$

This enables to estimate the ratio $k_7/\sqrt{k_6}$ as well as the effective rate of initiation w_{eff} and to compare it with the value of the initiation rate evaluated from the rate of decomposition of AIBN and thus to calculate the factor *fn*.

b) Graphical approach based on the experimentally determined ratio Q_t/Q_{stat} (modified Bamford-Bagdassaryan equation [30]) in the form:

$$-\frac{1}{\Phi}+\ln\frac{1+\Phi}{1-\Phi}=\frac{k_7 Q_{\mathrm{stat}}t}{\Delta HVk_2[\mathrm{RH}]}+A_{\mathrm{i}} \tag{15}$$

where

$$\Phi=\frac{Q_{\mathrm{t}}}{Q_{\mathrm{stat}}} \tag{16}$$

and A_{i} is a constant.

In Eq. (15), the Eqs (10)–(13) are combined with the analytical solution of Eq. (14).

The dependence of the left side of this equation on time *t* should be a straight line, from its slope the ratio k_7/k_2 can be obtained. However, as it can be seen from the Bagdassaryan-Bamford transformation of the experimental curves for oxidation of cumene (Fig. 6), the linearity holds only for a limited section of the above graphs. This approach thus may involve some error in determination of the rate constant k_7 depending on the selection of the proper part of the transformed line. By further analysis of Bagdassaryan-Bamford transformation we have found that the realistic values of the rate constant of inhibition are obtained when a steeply increasing part of the curve is involved in the evaluation.

From this viewpoint non-linear regression analysis of the experimental curves yields better coincidence with the theoretical assumption.

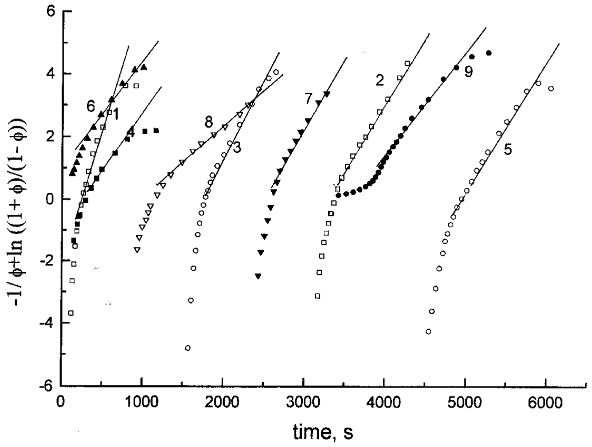


Fig. 6 Bamford-Bagdassaryan metamorphosis of the lines 1–9 of Fig. 1 for the oxidation of cumene at 60°C

Provided that the rate constants k_6 and k_2 are available, the described procedure allows for the calculation of the rate constant of the inhibitor interaction with propagation free radicals ($R^{\cdot}$ or $RO_2^{\cdot}$) either in the case of oxidation of cumene or polymerization of styrene.

For determination of k_7 constants for inhibited oxidation of cumene and polymerization of styrene the following parameters were used:

inhibited oxidation of cumene	inhibited polymerization of styrene
k_6=1.9·10^4 l mol^{-1}s^{-1} [31]	k_6=7.2·10^7 l mol^{-1}s^{-1} [31]
k_2=1.75 l mol^{-1}s^{-1} [32]	k_2=176 l mol^{-1}s^{-1} [31]
V=4 ml	V=4 ml
[RH]=6.9 mol l^{-1}	[RH]=8.26 mol l^{-1}
ΔH=114 kJ mol^{-1}	ΔH=67.3 kJ mol^{-1}

Q_{stat}=values in Tables 2 and 3

The rate of initiation w_i was calculated using parameters for AIBN decomposition published in [27].

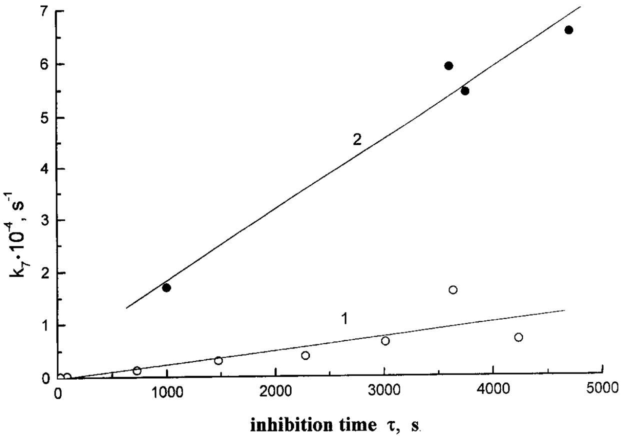


Fig. 7 Correlation between the rate constant k_7 of inhibition for oxidation of cumene (line 1) and polymerization of styrene (line 2) at 60°C

The values of $k_7/(fn)$ for both the oxidation of cumene and polymerization of styrene which were obtained by the two approaches are presented in Tables 2 and 3. The correspondence between the values of k_7 and inhibition time τ is obvious (Fig. 7). It is worth of mentioning that the values of fn are lower than 1 for all benzoquinones examined for both the oxidation and polymerization. When compared to ionol for which fn is approximately 1.8, benzoquinone amines ineteracting either with peroxyl radicals during oxidation or with alkyl radicals during polymerization yield free radicals potentially still capable of propagating the kinetic chains. It appears that benzoquinone amines are relatively good inhibitors of the polymerization of styrene (the transfer rate constant of alkyl radicals to the inhibitor is of the order 10^4 l mol^{-1}s^{-1}) while they act as relatively weak inhibitors or oxidation of cumene (the rate constant k_7 is by one order lower than that in polymerization).

Conclusions

1. The solution microcalorimetry proves to be an excellent method for the estimation of antioxidative efficiency of inhibitors in free radicals reactions of polymerization and oxidation.

2. The rate constants of elementary reactions of peroxy or alkyl radicals with inhibitors may thus be determined which are in a good agreement with the results obtained by other methods.

* * *

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