The activation of amines of various structures in synergistic mixtures with quinones during the retardation of polymerization of methyl methacrylate

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The retardation of the radical polymerization of methyl methacrylate (MMA) mixed with quinones (Q) is accompanied by activation of amines of various structures (InH). In the absence of quinones, primary amines (α-naphthylamine), secondary amines (diphenylamine, *N*-phenyl-β-naphthylamine, dimethyl-bis-*p*-(phenylaminophenoxy)silane, *N,N'*-diphenyl-*p*-phenylenediamine, and *N*-phenyl-*p*-aminophenol), and tertiary amines (*N,N,N',N'*-tetramethylethylenediamine and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine) exert no effect on the process. In the presence of 2,3,5,6-tetrachloroquinone or *p*-benzoquinone, amines inhibit polymerization (synergism). The consumption of amines is due to the abstraction of mobile H-atoms from their molecules. The retatdation by tertiary amines occurs only in the case when a mobile H atom is present at the α-C atom of the amine; a mixture containing *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine is ineffective. Analysis of various kinetic schemes shows that the activation of amine and its participation in the reaction with growing MMA radicals may occur either through the formation of active inhibitory species incorporated in the donor-acceptor complex, [InH · Q], or by inhibitory radicals, In$^\cdot$ and QH$^\cdot$, generated by the transfer of an H-atom from InH to Q.

Key words: retardation of polymerization, synergism, mixtures of inhibitors; primary, secondary, and tertiary aromatic amines, quinones.

Previously[1] we discovered the synergistic action of binary mixtures of amines with quinones in the oxidation of hydrocarbons and showed that the efficiency of retardation increases as [O_2] in the oxidizing gas decreases. Later, considering radical polymerization as a process that occurs practically in the absence of oxygen, we studied[2] the effects of these binary mixtures (diphenylamine or *N,N,N',N'*-tetraethyl-*p*-phenylenediamine with 2,3,5,6-tetrachloroquinone) on the polymerization of methyl methacrylate (MMA), and also observed their synergistic behavior. Since we have already shown the possibility of using non-reactive amines for retarding polymerization, the purpose of the present work has been to extend the range of amines and to elucidate the mechanism of their activation.

A little data on the effects of amines on the efficiency of the action of quinones in similar processes has been reported.[3,4] In these works, no direct evidence of the transformation of amines is given. Moreover, different suggestions concerning the role of amines have been stated. In particular, it is believed that amines are not consumed in the reaction, but only catalyze it.[3]

In the present work we have shown that during the retardation of polymerization, amines mixed with quinones behave similarly to inhibitors of oxidation, *i.e.*, they are consumed through the abstraction of the mobile hydrogen atom from the amino group.

Experimental

The radical polymerization of MMA initiated by azobisisobutyronitrile ($2 \cdot 10^{-3}$ *M*) was carried out in the absence of oxygen at 60 °C. The rate of initiation (W_i) was $2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1}. The efficiency of the retarding action of additives was evaluated using the kinetic curves of the variation of the degree of conversion (*C*) obtained by dilatometry.

Concentrations of the inhibitors were determined by spectrophotometry on the basis of the color, which results from azo coupling with diazotated *p*-nitroaniline in an acid medium in the case of *N*-phenyl-β-naphthylamine (535 nm), or from the reaction of amine with concentrated H_2SO_4 in the case of diphenylamine (608 nm). The concentration of quinonediimine, *viz.*, the product of the transformation of *N,N'*-diphenyl-*p*-phenylenediamine, was determined at 476 nm.

Quinonediimine was identified by TLC on Silufol UV-254 plates using a specially prepared solution of quinonediimine as a reference spot. A hexane : benzene : ether, 6 : 4 : 3 (v/v), solvent mixture was used as the mobile phase.

MMA was purified by successive treatment with 30 % aqueous solutions of $FeSO_4$ and KOH, then washed with water

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to neutral reaction, dried with $CaCl_2$, and distilled *in vacuo* at 33 °C (50 Torr).

Results and Discussion

The effects of separate components and mixtures of quinones (Q) with amine inhibitors (InH) on the radical polymerization of MMA is shown in Fig. 1. Inhibitors InH of various structures — primary α-naphthylamine (α-HA), secondary amines, *viz.*, diphenylamine (DPA), dimethyl-bis-*p*-(phenylaminophenoxy)silane (S-1), *N,N'*-diphenyl-*p*-phenylenediamine (DPPD), and *N*-phenyl-*p*-aminophenol-hydroxydiphenylamine, and tertiary amines, *viz.*, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPDA) — taken one at a time do not change the rate of polymerization of MMA. The kinetic curves recorded with and without these additives coincide (see Fig. 1, *a*, straight line *1*). This result comes as no surprise, since aromatic amines (primary or secondary) that act as oxidation inhibitors and are characterized by large rate constants of the reactions with peroxy radicals (k_7) exhibit low reactivities toward alkyl radicals.[5–7] 2,3,5,6-Tetrachloroquinone (chloranil (CA)), taken alone also has no effect on the rate of the process (curve *1*) due to the low value of the rate constant of CA reaction with growing MMA radicals, which is only 120 L mol^{-1} s^{-1} (44.1 °C).[8] Mixtures of inhibitors (see Fig. 1, *a*, curves *2—8*) noticeably decelerate polymerization. The mixture of *p*-benzoquinone with DPA (Fig. 1, *b*, curve *3*) also has a greater effect than *p*-benzoquinone alone (curve *2*). Thus, we observe the synergistic action of amines of various structures with quinones, which is probably due to activation of one or both components.

The activation of an amine in a mixture should result in its consumption; this has been experimentally confirmed. In fact, *N*-phenyl-β-naphthylamine (neozone-D) taken alone is not consumed (Fig. 2, curve *1'*) and does not decelerate polymerization (see Fig. 2, curve *1*). When neozone-D is introduced together with CA, it is consumed (curve *2'*) and the rate of polymerization decreases (curve *2*). Similar results have been obtained for DPA and DPPD (Table 1).

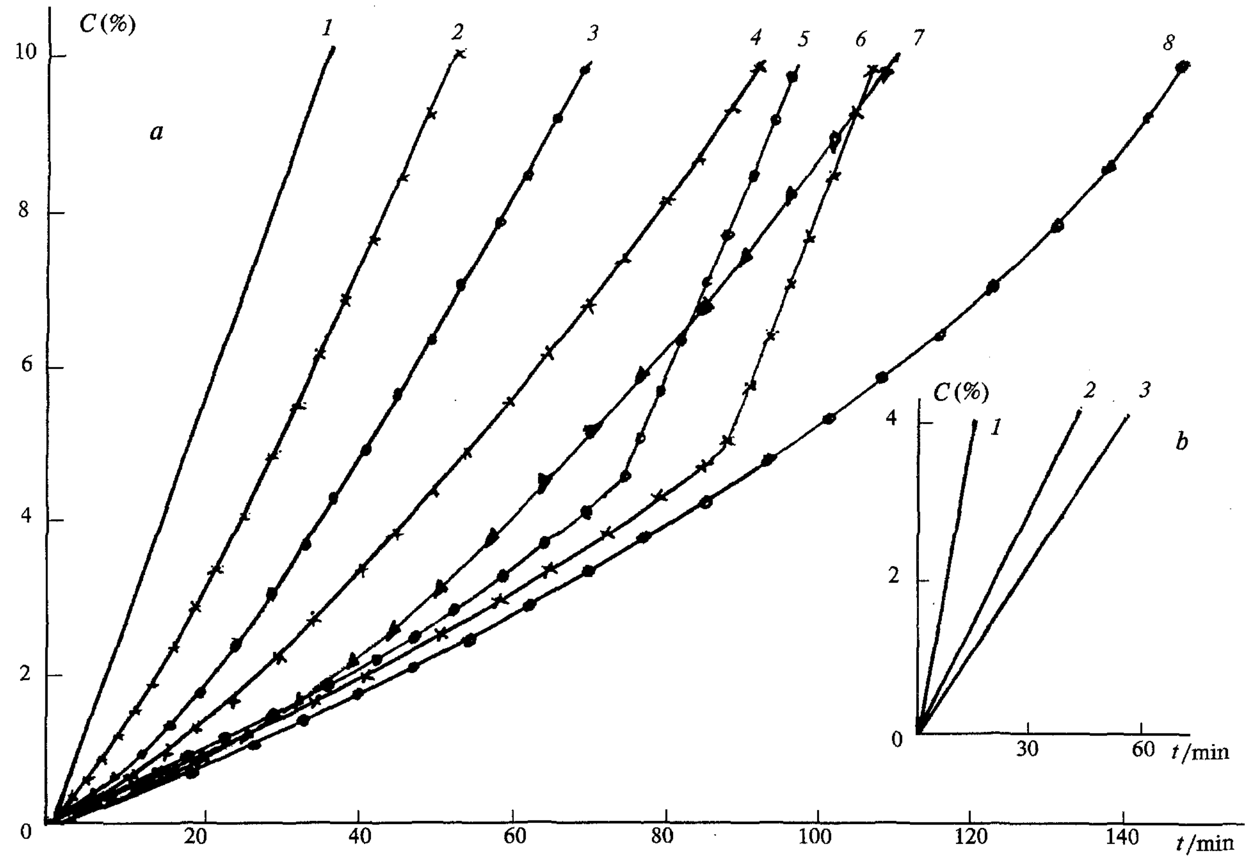


Fig. 1. *a*. The kinetic curves of polymerization of MMA without additives and in the presence of $2 \cdot 10^{-3}$ *M* CA or $5 \cdot 10^{-4}$ *M* InH (*1*) and of CA mixtures with various InH (*2—8*): α-HA (*2*), DPA (*3*), TMEDA (*4*), DPPD (*5*), S-1 (*6*), hydroxy-DPA (*7*), TMFDA (*8*). *b*. The same without additives (*1*) and in the presence of: $2 \cdot 10^{-3}$ *M* DPA (*1*); $1.2 \cdot 10^{-3}$ *M* *p*-benzoquinone (*2*); a mixture of $1.2 \cdot 10^{-3}$ *M* *p*-benzoquinone and $2 \cdot 10^{-3}$ *M* DPA (*3*) (60 °C, $W_i = 2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1}).

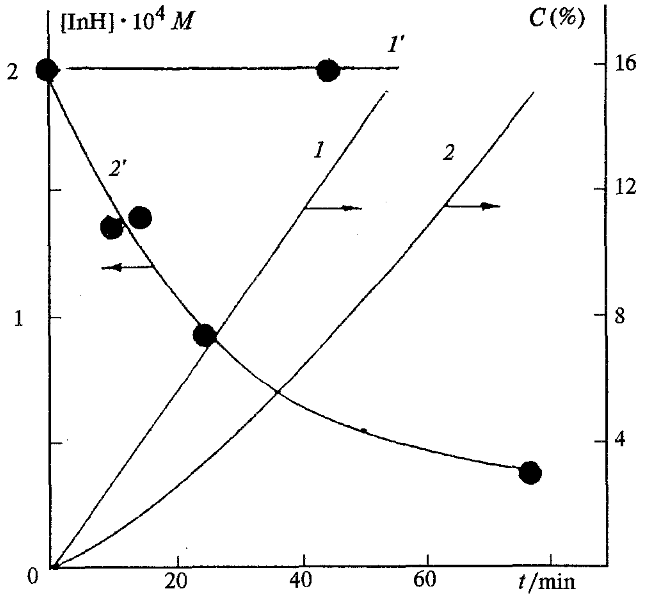


Fig. 2. The kinetic curves of polymerization of MMA (*1, 2*) and consumption of *N*-phenyl-β-naphthylamine (*1', 2'*) without additives (*1, 1'*) and in the presence of $2 \cdot 10^{-3}$ *M* CA (*2, 2'*). The points on curve *2'* are experimental (60 °C, W_i = $2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1}), the solid line is the calculated dependence.

Table 1. Kinetics of the consumption of inhibitors (InH) during the retardation of the radical polymerization of methyl methacrylate by InH—chloranil mixtures (60 °C, W_i = $2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1})

InH	$[InH]_0 \cdot 10^4$ /*M*	$[XA]_0 \cdot 10^3$ /*M*	Duration of the reaction, *t*/min	$[InH]_t \cdot 10^4$ /*M*
DPA	2.0	2.0	15	1.44
	2.0	2.0	45	1.14
	2.0	—	35	2.0
DPPD	5.0	2.0	95	0.85*
	14.0	—	40	14.0

* The concentration of the quinodiimine formed was $4.15 \cdot 10^{-4}$*M*.

Table 2. The retardation of the radical polymerization of methyl methacrylate (W_0/W_{inh}) by mixtures of amines (InH) with chloranil (CA)

InH	W_0/W_{inh}	$k_7 \cdot 10^4$ /L mol^{-1} s^{-1}	Reference
α-Naphthylamine	1.9	1.4	9
Diphenylamine	3.7	4.4	9
N,N'-Diphenyl-*p*-phenylenediamine	5.8	200	9
p-Hydroxydiphenylamine	6.6	100	9
Dimethyl-bis-*p*-(phenylaminophenoxy)silane	7.0	8.4	10

Note. $[CA]_0 = 2 \cdot 10^{-3}$ *M*, $[InH]_0 = 5 \cdot 10^{-4}$ *M*; $W_i = 2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1}, 60 °C.

The activation of amine and its interaction with growing PMMA radicals ($P_n^{\cdot}$) is indicated by the fact that the efficiency of the retardation of the polymerization (W_0/W_{inh}, where W_0 and W_{inh} are the rates of polymerization without additives and in the presence of an InH—Q mixture, respectively) increases when k_7 increases (Table 2).

This dependence is linear for inhibitors of the same type of action: primary amine (α-HA), secondary monoamine (DPA), and diamine (S-1), whose amino groups are separated by a silicon atom and probably act independently from one another. Notice that the data for DPPD and hydroxy-DPA, which possess the highest antiradical activities (see Table 2, compounds **3** and **4**), do not correspond to a linear dependence; these compounds retard polymerization to a lesser degree. This result may be attributed to the peculiarities of the mechanism of the action of compounds **3** and **4** compared to that of monoamines, namely, the decay of only two reactive chains, in spite of the presence of two amino groups, and the formation of quinoid products.

In Table 3 the values for the initial rate of polymerization in the presence of binary mixtures containing CA and various aromatic amines are compared with the literature[11] values for the ionization potentials (*I*) of the corresponding amines. One can see that the more easily the transfer of an electron from the amine molecule occurs, the higher the efficiency of the inhibition. These data make it possible to infer that the mechanism of the activation of amines involves donor-acceptor interaction of amines with quinones.

This donor-acceptor interaction[12] for mixtures of CA with α-HA, DPA, and *N,N,N',N'*-tetraethyl-*p*-phenylenediamine was detected on the basis of the appearance of a new band in the absorption spectra.[2] For example, for a CA—DPA mixture in MMA, the following characteristics of the [DPA · CA] complex were obtained: λ = 635 nm, ε = 1330 L mol^{-1} sm^{-1}, K_e = 0.35 L mol^{-1} (20 °C).

To verify the mechanism suggested for the activation of amine, which involves the formation of a donor-acceptor complex that reacts with the $P_n^{\cdot}$ radicals, let us compare the calculated and experimental kinetic data

Table 3. The values of the ionization potentials (*I*) of amines[11] and the initial rates of polymerization (W_{inh}) of methyl methacrylate inhibited by mixtures of amines with chloranil

Amine	$W_{inh} \cdot 10^3$ /%*C* s^{-1}	*I* /eV
α-Naphthylamine	2.5	7.3
Diphenylamine	1.3	7.14
N,N,N',N'-Tetramethyl-*p*-phenylenediamine	0.6	6.18

Note. $[Amine]_0 = 5 \cdot 10^{-4}$ *M*, $[CA]_0 = 2 \cdot 10^{-3}$ *M*, W_i = $2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1}, 60 °C.

for the consumption of amine in a CA—neozone-D mixture (see Fig. 2, *a*, curve *2*). The reactivity of the complex is described by the equation[2]

$$\frac{W_0}{W_{\text{inh}}} - \frac{W_{\text{inh}}}{W_0} = \frac{fk_{\text{inh}}K_{\text{e}}[\text{InH}]_0[Q]_0}{\sqrt{k_4W_i}}, \qquad (1)$$

where f is the stoichiometric coefficient of inhibition, k_{inh} and k_4 are the rate constants of chain termination on the complex and quadratic self- termination, respectively, K_{e} is the equilibrium constant of complex formation.

Let us assume that at instant t the concentration of the inhibitor consumed is X. Then

$$([\text{InH}]_0 - X)([\text{Q}_0] - X) = \left(\frac{W_0}{W_{\text{inh}}} - \frac{W_{\text{inh}}}{W_0}\right)\cdot\frac{\sqrt{W_{\text{i}}k_4}}{fk_{\text{inh}}K_{\text{e}}}.$$

The value of X can be determined by solving the quadratic equation and amounts to:

$$X = \frac{([\text{InH}]_0 + [\text{Q}]_0) - \sqrt{([\text{InH}]_0 + [\text{Q}]_0)^2 - 4([\text{InH}]_0[\text{Q}]_0 - B)}}{2},$$

where $B = \left(\sqrt{k_4W_{\text{i}}} / fk_{\text{inh}}K_{\text{e}}\right)\cdot(W_0 / W_{\text{inh}} - W_{\text{inh}} / W_0)$.

The value of $fk_{\text{inh}}K_{\text{e}}$, equal to $2.15 \cdot 10^7$ L^2 mol^{-2} s^{-1}, was determined from the initial section of the polymerization curve using Eq. (1). The W_{inh} values for the calculation of B were determined from the same equation at various instants. The calculated kinetic curve of the consumption of neozone-D is shown in Fig. 2 by the solid line (curve *2'*). One can see that it conforms to the experimental points.

Thus, the activation of an amine by binding it into a complex that is reactive with respect to the growing alkyl radicals, is in satisfactory agreement with the experiment.

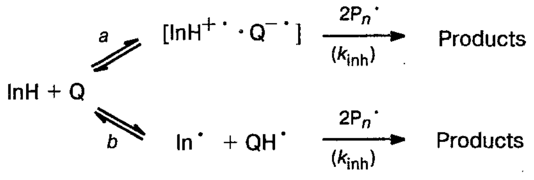
The activation is accompanied by the abstraction of the active hydrogen from the amine molecule. This is confirmed by the correlation between W_0/W_{inh} and k_7 for primary and secondary aromatic amines given in Table 2, by the accumulation of the product of the transformation of DPPD, quinodiimine, which was identified by absorption spectroscopy and TLC, and also by the data on the retardation of polymerization by mixtures involving tertiary amines. The efficiency of the retardation of the radical polymerization of methyl methacrylate (W_0/W_{inh}) by mixtures of chloranil with tertiary amines ($[\text{CA}]_0 = 2 \cdot 10^{-3}$ *M*, $[\text{Amine}]_0 = 5 \cdot 10^{-4}$ *M*, $W_{\text{i}} = 2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1}, 60 °C) is given below.

Tertiary amine	W_0/W_{inh}
N,N,N',N'-Tetramethylethylenediamine	3.5
N,N,N',N'-Tetramethyl-*p*-phenylenediamine	7.6
N,N,N',N'-Tetraphenyl-*p*-phenylenediamine	1.0

One can see that the tertiary aromatic amine, *N,N,N',N'*-tetraphenyl-*p*-phenylenediamine, which contains no active hydrogen atoms at the α-carbon atom, does not retard the radical polymerization of MMA and the kinetic curve of the accumulation of the polymer in the presence of this mixture coincides with the curve of polymerization without additives. Thus, the activation of amine necessarily involves abstraction of hydrogen. Not only active hydrogen from the amino groups of primary and secondary amines, but also a hydrogen atom at the α-carbon atom of the substituents (CH_3, C_2H_5) in tertiary amines can participate in the reaction.

The view that amine is consumed through elimination of a H atom is supported by the magnitudes of the stoichiometric coefficients f calculated for three aromatic amines. The f coefficients were attributed to the action of an active species produced by the interaction of the components of the mixture. If one assumes that the concentration of the active species is equal to the concentration of the amine, which is deficient, then the value of f for the mixture with DPA will be 2.5, with DPPD it will be 2.1, and with neozone-D it will be 2—2.5. The stoichiometric coefficients for the two former amines were calculated from the kinetic curves of polymerization, that for neozone-D was found from the kinetic curves of its consumption at various initial concentrations.

The resulting values for f are close to the values of stoichiometric coefficients observed for the above-listed aromatic amines when they decelerate oxidation, which is known to be accompanied by abstraction of the H atom from the NH group. The f values close to 2 may refer equally to alternative schemes of the process, for example



Mechanism *a*, which describes the kinetics of the consumption of amine, is in satisfactory agreement (Fig. 3, straight line *1*) with the experimental dependence of the initial rates of polymerization on the product of the concentrations of the starting components of the CA—DPA mixture, in conformity with Eq. (1).

The inhibition of the polymerization of MMA according to mechanism *b* was observed by us previously[12] for a mixture of 3,6-di-*tert*-butylpyrocatechol (QH_2) with the corresponding quinone (Q). The retardation occurs[13] through the reaction of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl radicals (QH$^\cdot$) with the growing polymer radicals, QH$^\cdot$ + P$_n{}^\cdot$ → products, and the depen-

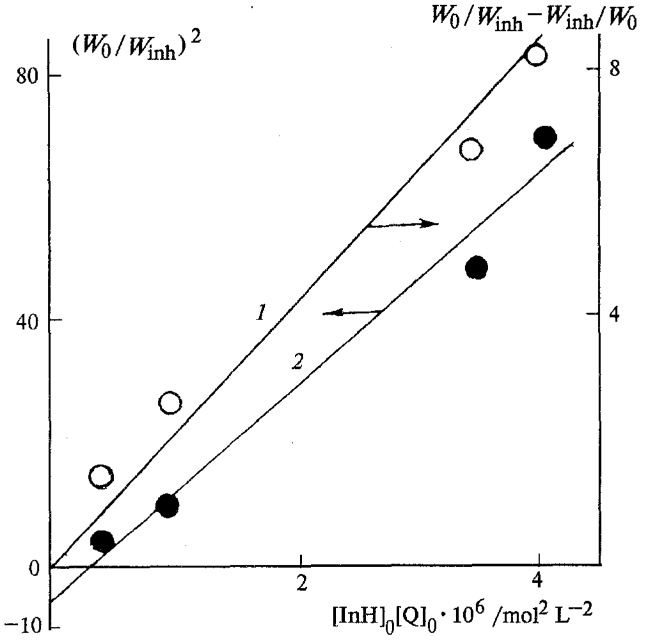


Fig. 3. The dependence of the initial rate of polymerization of MMA inhibited by a DPA—CA mixture on the product of the initial concentrations of components in the coordinates of Eq. (1) (*1*) and (2) (*2*) (60 °C, $W_i = 2.4 \cdot 10^{-7}$ mol L^{-1} s^{-1}).

dence of the initial rate of polymerization on the initial concentration of the starting components is described by the following equation:[12]

$$(W_0 / W_{inh})^2 = -k^2_{inh} / k_4 k_d + (k^2_{inh} K_e / k_4 W_i) \cdot [Q]_0[QH_2]_0, \quad (2)$$

where k_d is the rate constant of disproportionation of $QH^{\cdot}$, $K_e = k_{-d}/k_d$, where k_{-d} is the rate constant of the formation of the $QH^{\cdot}$ radicals. Only one type of the inhibitor radicals, *viz.*, $QH^{\cdot}$, participates in the reaction.

Let us consider whether the regularities observed for inhibition by an (InH—Q) mixture that forms two types of radicals derived from the inhibitors, $In^{\cdot}$ and $QH^{\cdot}$, can be explained by a similar mechanism (path *b*). In the case of different radicals, it is difficult to carry out a calculation similar to that given above. For the sake of simplicity, we assumed that these radicals possess equal reactivities and cannot be distinguished. This allowed us to use Eq. (2). In terms of the assumption made, we evaluated the applicability of mechanism *b* to a mixture of DPA with CA. Figure 3 presents the satisfactory linearization (straight line *2*) in the coordinates of Eq. (2), where the tangent of the slope is $k^2_{inh}K_e/k_4W_i$ = $1.6 \cdot 10^7$ L^2 mol^{-2}, and the intercept on the ordinate axis is k^2_{inh}/k_4k_d = 5. From the data obtained, taking into account the reported[14] value, $k_4 = 3.7 \cdot 10^7$ L mol^{-1} s^{-1}, we found that the rate constant of the formation of the inhibitory radicals, k_{-d}, is 0.8 L mol^{-1} s^{-1}. This value is in good agreement with the value of this constant for a 3,6-di-*tert*-butylpyrocatechol—3,6-di-*tert*-butyl-*o*-benzoquinone mixture, which is equal to[12] 1 L mol^{-1} s^{-1}.

Despite the assumption made in the calculation that the reactivities of the $In^{\cdot}$ and $QH^{\cdot}$ radicals are equal, one can resort to mechanism *b* to explain the action of mixtures of amines with quinones. Therefore, we do not prefer either of the mechanisms.

Simultaneous inhibition by the complex and by the radicals formed also cannot be ruled out. This is also supported by the reported ESR data[15] that in frozen solutions of InH—Q systems, the transfer of an electron through the action of light occurs in parallel with the transfer of hydrogen.

Thus, the use of amines mixed with quinones makes it possible to extend the field of application of the traditional amine antioxidants and to use them for retarding radical polymerization occurring in the absence of oxygen.

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