Kinetic description of the oxidation of hydrocarbons inhibited by sulfur-containing hydrogenated quinolines

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The inhibiting effect of dithiolthione derivatives of hydrogenated quinolines (DTT) on the oxidation of various hydrocarbons (*n*-decane, *n*-decene, ethylbenzene, β -carotene) was investigated. The inhibiting effect of the DTTs is greater at high temperatures (>100 °C) than that of the parent hydrogenated quinolines and weaker at moderate temperatures. The DTTs do not affect the decomposition of hydroperoxides. Probably, the introduction of a dithiolthione cycle to a hydroquinoline molecule decreases its reactivity toward O₂ and peroxide radicals, which favors the enhancement of the antioxidative activity of the DTTs at elevated temperatures.

Key words: hydrogenated quinolines, dithiolthione derivatives; *n*-decane, *n*-decene, ethylbenzene, β -carotene, inhibited oxidation.

Hydrogenated 2,2,4-trimethyl-substituted quinolines (HO) are amine-type antioxidants, of which acetonanil and ethoxyquin¹ are known the best. The HQs are efficient inhibitors of the oxidation of hydrocarbons of various classes including unsaturated hydrocarbons,² but the inhibiting effect at elevated temperatures is not high.³ The inhibiting action of HQs depends significantly on the type of substituent in the aromatic ring and on the degree of hydrogenation of the heterocycle.⁴⁻⁶ Sulfur-containing inhibitors are known to efficiently inhibit oxidation at high temperatures.⁷ It was therefore interesting to study HQ derivatives that contain, along with the >NH group, a sulfur-containing fragment. In the present work we estimated the inhibiting action of novel sulfur-containing hydrogenated quinolines in the oxidation of hydrocarbons belonging to various classes over a wide temperature range. We varied the oxidation conditions and the substrates, which allowed us, based on comparative phenomenological data, to draw some conclusions about the particular features of the mechanism of the antioxidative action of these compounds.

Experimental

Dithiolthione derivatives of dihydroquinoline (DTT) were obtained by boiling the respective 6-R-2,2,4-trimethyl-1,2-dihydroquinolines (1a-d) with sulfur in DMF⁸ (Scheme 1). DTT 2a was transformed into dithiolthiones 2e, 2f, and 3 by nitration with nitric acid ($\rho = 1.4 \text{ g cm}^{-3}$) in acetic acid, by alkylation with triphenylmethanol, and by acetylation, respec-

tively. Condensation of 2a methiodide with aniline gave imine 4 which was transformed by acid hydrolysis into compound 5 (see Scheme 1). The parameters of compounds 2a-d agree with the literature data.⁹ The properties of DTT 2e, 2f, 4, and 5 are presented in Table 1. Dimer 6 was obtained similarly to compounds 2 from the respective dimer of acetonanil. The compounds were purified by repeated crystallization from toluene and ethanol. The purity of the compounds was monitored by TLC.

The hydrocarbons (RH) were oxidized in thermostated bubbling-type vessels in a stream of oxygen or air (1.6 L h⁻¹) or in the oxidating cell of a gasometric setup at $p_{O_2} = 1$ atm. *n*-Decane (at 150 °C), *n*-decene (120 °C), ethylbenzene (60 °C), and a polyenic hydrocarbon, β -carotene (50 °C), were used as substrates for oxidation. The oxidation rate was monitored by the accumulation of hydroperoxides, whose content was measured by the iodometric method (*n*-decane, *n*-decene), by oxygen absorption (ethylbenzene), or by hydrocarbon consumption (β -carotene⁶).

n-Decane and ethylbenzene were purified according to standard procedures. *n*-Decene (grade "pure") and β -carotene (Hoffmann-LaRoche, Basel, Switzerland) were used without additional purification.

Results and Discussion

The oxidation of *n*-decane can be a model reaction for a comparative estimation of the inhibiting action of various antioxidants during the oxidation of a wide range of oil products at elevated temperatures. The accumulation of hydroperoxides (ROOH) at 150 °C occurs with self-acceleration (Fig. 1, curve I), and the kinetic curve has a parabolic shape. When oxygen is replaced by air

Translated from Izvestiya Akademii Nauk. Seriya Khimicheskaya, No. 5, pp. 814-818, May, 1994. 1066-5285/94/4305-0755 \$12.50 © 1995 Plenum Publishing Corporation



R = H (a), Me (b), OMe (c), OEt (d), NO₂ (e), CPh₃ (f)

(curve 1'), the reaction rate during the initial period of the process almost does not change, *i.e.*, the initiation of oxidation chains occurs mostly due to the thermal de-

composition of ROOH. Probably, the relative deceleration of the accumulation of ROOH when air is bubbled ([ROOH] $> 5 \cdot 10^{-2}$ mol L⁻¹) results from the more

DTT	M.p./°C	Yield (%)	Found Calculated N	Mol. mass	Molecular formula	IR, v/cm^{-1}	
						>NH	C=S(O, N)
2e	237-238	40	<u>9.21</u> 9.02	310	$C_{12}H_{10}N_2O_2S_3$	3380, 1345*	1227, 1630
2f	270—271	45	<u>2.93</u> 2.76	507	$C_{31}H_{25}NS_3$	3400	1230
4	131-132	65	<u>8.38</u> 8.50	323	$C_{18}H_{15}N_2S_2$	3320	1620
5	145—146	30	<u>5.91</u> 5.62	249	$C_{12}H_{11}NOS_2$	3330	1630

Table 1. Physicochemical parameters of the DTT synthesized



Fig. 1. Kinetic curves of ROOH accumulation during the oxidation of *n*-decane in the absence (1, 1') and in the presence of inhibitors (2-11): 2, 1a; 3 and 3', 1d; 4, 3; 5, 2a; 6, 2b; 7, 2e; 8 and 8', 2d; 9, 7; 10, 6; 11, ionol. [InH]₀ = $2 \cdot 10^{-4}$ mol L⁻¹, 150 °C; 1-11, in O₂; 1', 3', and 8', in the air.

intense decomposition of ROOH when the concentration of oxygen is decreased.

The comparison of the inhibition periods (τ) caused by the addition of acetonanil (1a) and ethoxyquin (1d) (see Fig. 1, curves 2 and 3, respectively) as well as the sulfur-containing (curves 5-8) and 6-hydroxysubstituted (7) HQ analogs shows that the introduction of both a dithiolthione ring and an OH group in an HQ molecule significantly increases the antioxidative effect in the system studied. It is remarkable that the inhibition time in the presence of a DTT is practically independent of the nature of the substituent R. There is only one NO₂-containing compound 2e which shows no significant inhibiting effect. The comparison of $\boldsymbol{\tau}$ values obtained at higher inhibitor concentrations $([InH]_0 =$ $4.5 \cdot 10^{-4}$ mol L⁻¹) demonstrates that the addition of compounds 4 or 2f decreases the inhibition time by ca. 10 % compared to that in the case of DTT 2a.

Dimer $\mathbf{6}$ is the most efficient inhibitor of the DTTs studied (cf. Ref. 12). One can see from Fig. 1 that the inhibition period in the presence of this dimer is almost twice as long as in the presence of compound 2a, although it contains only one dithiolthione ring. This may result from the presence of two hydroquinoline moieties in molecule 6 and, hence, to some extent, from an increase in the stoichiometric coefficient of inhibition. Furthermore, oxidation in an open vessel or with bubbling oxygen or air at elevated temperatures significantly depends on the volatility of the inhibitor, which normally decreases with an increase in the molecular mass. Therefore, other conditions being equal, oligomeric antioxidants, which are more efficient due to their better retention in the system, are more convenient in practical use.

The inhibition periods in the presence of all DTTs are several times shorter than in the presence of the same amounts (in mol L^{-1}) of a hindered phenol, ionol (see Fig. 1, curve 11). This fact indicates that a DTT that participates in breaking the chains involving RO_2^{-1} , is also markedly consumed through other pathways (in reactions with O_2 , ROOH, etc.).

The inhibition effects of DTTs are stronger than those of HQs, which may be due to the following factors: a) participation of the sulfur-containing moiety in chain breaking, *i.e.*, an increase in the stoichiometric factor of chain breaking (f); b) participation of DTT in the decomposition of hydroperoxides (a typical reaction of sulfur-containing inhibitors⁷) and the resulting decrease in the rate of the chain initiation (w_i) ; c) higher anti-radical activity of DTT, *i.e.*, a higher rate constant of the reaction of the inhibitor with $RO_2^{-}(k_{in})$; d) a change in the reactivity of the aminyl radical, namely, an increase in its stability with respect to the elimination of the methyl group occurring at elevated temperatures.³

The stoichiometric coefficient of chain breaking, determined for DTTs by the standard method based on the duration of the inhibition periods in ethylbenzene oxidation initiated by azobisisobutyronitrile (AIBN)¹⁰ (Table 2), does not exceed f for the corresponding HQs:⁴

$$f = w_i \tau / [\text{InH}]_0 = 1.3 \div 1.4.$$

The kinetic curves of oxygen absorption in the presence of DTTs are similar to those obtained in the presence of HQs:^{4,11} when an inhibition period comes to an end, the rate of O_2 absorption is almost equal to that of the non-inhibited process. The addition of DTT 2e, which contains a NO₂ group at the aromatic ring, does not change the oxidation rate, just like the corresponding HQ.⁵ Compound 3, in which a hydrogen atom in the amino group is replaced by an acetyl group, does not affect the oxidation of ethylbenzene and *n*-decane (see Fig. 1, curve 4). It follows from the combined body of these data that the dithiolthione moiety itself is not an acceptor of radicals.

Direct experiments (Fig. 2) showed that small DTT additions, which are used for the inhibition of *n*-decane oxidation $(10^{-4}-10^{-3} \text{ mol } \text{L}^{-1})$, do not affect the thermal decomposition of hydroperoxide. It is necessary to note that DTTs are colored compounds, which, unlike HQs, have a characteristic absorption band in the visible spectrum region at 405–460 nm (depending on the type of substituent R). It is convenient to monitor the consumption of a DTT by measuring the changes in the intensity of this band. As seen from Fig. 2, the rate of consumption of compound **2a** is proportional to [ROOH]₀ but is much less than the rate of ROOH decomposition: $w_{\text{DTT}}/w_{\text{ROOH}} = 0.05$.

Table 2. Determination of the stoichiometric inhibition factor (f) for a series of DTTs (ethylbenzene, $w_i = 5 \cdot 10^{-7} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$, 60 °C)

DTT	$[InH] \cdot 10^4 / mol L^{-1}$	τ/min	f	
2a	4.15	18	1.3	
2a	8.30	36	1.3	
2d	4.15	18	1.3	
2e	8.10	0		
5	4.00	19	1.4	



Fig. 2. Kinetics of the consumption of *n*-decyl hydroperoxide (1, 2) and DTT **2a** (3) at 150 °C in an atmosphere of nitrogen ("special purity"); 1, consumption of ROOH without additives, [ROOH]₀ = $3 \cdot 10^{-2}$ mol L⁻¹; 2, the same in the presence of **2a** ($2 \cdot 10^{-3}$ mol L⁻¹); 3, dependence of the initial rate of the consumption of **2a** on [ROOH]₀, [**2a**]₀ = $2.5 \cdot 10^{-3}$ mol L⁻¹.

Thus, the sulfur atoms of the dithiolthione moiety in a DTT molecule are not acceptors of radicals and do not significantly affect the decomposition of ROOH. Most probably, the increased antioxidative action of the DTTs (in comparison with the HQs) originates from a change in the electron environment of the nitrogen atom and, hence, the anti-radical activity of the DTTs and the reactivity of the aminyl radicals formed from the DTTs. The trend in the changes in the anti-radical activity of the DTTs in comparison with that of the HQs can be qualitatively estimated by testing the inhibiting effect of these compounds during the oxidation of a polyenic hydrocarbon, B-carotene, since in this case the inhibition times in the presence of HQs correlate with the constants of the reaction of the HQs with RO2[•] (cf. Ref. 4). It turned out that the inhibition periods during the oxidation of β -carotene in the presence of ionol, 1d, and 2d are 30, 200, and 80 min, respectively, while in the absence of inhibitor this period is 30 min (50 °C, benzene as the solvent, $[InH]_0 = 2.5 \cdot 10^{-5} \text{ mol } L^{-1}$, $[\beta$ -carotene]_0 = $6 \cdot 10^{-3} \text{ mol } L^{-1}$). According to these data, the inhibition period in the presence of DTT 2d has an intermediate duration between those for ionol and ethoxyquin: 1d > 2d > ionol. Thus, it can be assumed that $10^6 \mod L^{-1} s^{-1} > k_{in}(2d) >$ 10^4 mol L⁻¹ s⁻¹, and the DTTs display a lower antiradical activity than the corresponding HQs.

At elevated temperatures, compounds 1d and 7 are mainly consumed due to the reaction with oxygen.^{3,6} The oxidation of compound 1d is enhanced by a chain process with the decay of the aminyl radical as the key step.³



This reaction affords an active radical CH₃⁺ participating in the chain propagation of the oxidation of the hydrocarbon and HQ. Figure 1 (curves 8 and 8') shows that the inhibition period in the presence of a DTT increases with a decrease in p_{O_2} . It can be assumed that the direct interaction of DTTs with O2 contributes to the consumption of the inhibitor. However, the sulfur-containing derivatives are less active in the reaction with RO₂[•] than the HQs and, probably, react more slowly with O_2 . As a rule, when the temperature is decreased, the fraction of the reaction with oxygen in the overall consumption of the inhibitor decreases sharply due to the difference in the activation energies. Therefore, the DTTs more efficiently inhibit the oxidation of hydrocarbons at elevated temperatures than the HQs, whereas the opposite relation is observed at moderate temperatures.

Summarizing the data on the inhibiting action of the DTTs for various hydrocarbons, it can be concluded that dithiolthione derivatives should be employed in systems characterized by high rates of chain initiation and propagation at elevated temperatures. Industrial olefins can serve as examples of such systems.¹² For example, it is seen in Fig. 3 that DTT 6 provides a longer inhibition period in the oxidation of *n*-decene (initial content of peroxides $4 \cdot 10^{-3}$ mol L⁻¹) than ionol and the most active HQs. Hence, the reversal of the series of the



Fig. 3. Kinetic curves of ROOH accumulation during the oxidation of *n*-decene in the absence (1) and in the presence of inhibitors (2-4): 2, 1d; 3, ionol; 4, DTT 6. $[InH]_0 = 2 \cdot 10^{-4}$ mol L⁻¹, 120 °C, bubbling of O₂.

inhibiting activity in comparison with the series for *n*-decane and β -carotene is observed: 1d < DTT < ionol in purified *n*-decane at 150 °C; 1d < ionol < DTT in industrial *n*-decene at 120 °C; ionol < DTT < 1d in β -carotene at 50 °C.

References

- 1. B. N. Gorbunov, Ya. A. Gurvich, and I. P. Maslova, *Khimiya i tekhnologiya stabilizatorov polimernykh materialov* [*Chemistry and Technology of Polymer Stabilizers*], Khimiya, Moscow, 1981, 369 p. (in Russian).
- T. V. Lobanova, O. T. Kasaikina, Yu. A. Ivanov, A. B. Shapiro, and A. B. Gagarina, *Dokl. Akad. Nauk SSSR*, 1979, 245, 643 [*Dokl. Chem.*, 1979, 245 (Engl. Transl.)].
- 3. T. D. Nekipelova and A. B. Gagarina, *Dokl. Akad. Nauk* SSSR, 1976, 231, 392 [*Dokl. Chem.*, 1976, 231 (Engl. Transl.)].

- 4. O. T. Kasaikina, Z. S. Kartasheva, T. V. Lobanova, I. F. Rusina, Yu. A. Ivanov, and A. B. Gagarina, *Neftekhimiya* [*Petroleum Chemistry*], 1982, **22**, 265 (in Russian).
- O. T. Kasaikina, A. B. Gagarina, Yu. A. Ivanov, E. G. Rozantsev, and N. M. Emanuel', *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1975, 2247 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, 24, No. 10 (Engl. Transl.)].
- 6. D. V. Fentsov, T. V. Lobanova, and O. T. Kasaikina, Neftekhimiya [Petroleum Chemistry], 1990, **30**, 103 (in Russian).
- 7. G. Scott and P. A. Shearn, J. Appl. Polym. Sci., 1969, 13, 1329.
- 8. Pat. 1040552, Great Britain.
- 9. G. P. Brown, J. Chem. Soc. (C), 1968, 1074.
- 10. N. M. Emanuel' and D. Gal, *Okislenie etilbenzola* [Oxydation of Ethylbenzene], Nauka, Moscow, 1984, 376 p. (in Russian).
- O. T. Kasaikina, T. V. Lobanova, and D. V. Fentsov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2219 [Bull. Acad. Sci. USSR, Div. Chem. Sci., 1983, 32, 2002 (Engl. Transl.)].
- 12. Pat. 1528772 USSR; Byul. Izobret., 1989, No. 46.

Received August 5, 1993