Redox properties of hydrogenated quinoline derivatives — inhibitors in oxidation processes of hydrocarbons

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Half-wave potentials of the one-electron electrochemical oxidation ($E_{1/2}{}^{ox}$) of hydroquinolines with different degrees of heterocycle hydrogenization as well as containing substituents of various natures in the benzene ring and heterocycle have been measured. Linear correlations between $E_{1/2}{}^{ox}$ and the values of the Hammett polar σ-constants for *m*- and *p*-substituents in dihydroquinolines and related sulfur-containing dithiolthiones were established. The character of the variation of $E_{1/2}{}^{ox}$ in the series of hydroquinolines was found to correlate with the characteristic features of the inhibiting action of these compounds in the liquid-phase oxidation of various hydrocarbons. However, in contrast to phenolic antioxidants for hydroquinolines, there is no dependence of the retardation period on $E_{1/2}{}^{ox}$in the oxidation of hydrocarbons at temperatures higher than 100 °C.

Key words: hydroquinolines, half-wave oxidation potentials, Hammett equation, antioxidants.

Derivatives of 2,2,4-trimethylsubstituted hydrogenated quinolines (HQ) are inhibitors of chain reactions of liquid-phase oxidation of organic substances by molecular oxygen.[1–4] The retardation effects occurring in their presence depend essentially on the structure of HQ (degree of hydrogenation, presence of substituents) as well as on the structure of the oxidizing substance and the oxidation conditions.[3–6] In the case of traditional inhibitors, the antioxidants of the phenolic type (PhOH), the rate constants (k_i) of the interaction between the inhibitors and the peroxyl radicals of the oxidizing substance ($RO_2{}^{\cdot}$), which to a large extent determine the empirical effect of the inhibiting action of phenols,[7,8] can be easily and reliably determined by various methods. The k_i values change noticeably as the structure of the phenols varies, which allows one to analyze the influence of the nature, number, and position of substituents in the inhibitor molecules on their reactivity. These correlations may be used for the directing selection and synthesis of new promising antioxidants.

For inhibitors of the amine type (>NH), the reliable determination of k_i is usually difficult, because of the high activity of the >NH themselves and of the products of their oxidative transformations in side reactions with the hydroperoxides that form in the system or in other processes.[9] As a result, there is considerable variation in the k_i values available in the literature, which makes it difficult to analyze the effect of the >NH structure on its reactivity.

Electrochemical methods (polarography, voltammetry on solid microelectrodes, etc.) allow one to obtain important information about the physicochemical properties of various compounds in solutions. The degree of resolution of these methods is enough to elucidate the fine effects of substituents on redox properties of organic compounds of various classes,[9–13] including antioxidants. It is known that electrochemical redox characteristics of compounds, for example, the half-wave potentials of electrochemical oxidation ($E_{1/2}{}^{ox}$), correlate with the values reflecting the reactivity of compounds in chemical reactions.[15,16] This fact is often used for the prediction of the activity of related compounds in a given reaction.

Aromatic amines and diamines are easily oxidized with the transfer of one electron and are characterized by low values of ionization potentials in the gaseous phase.[17] A redox mechanism involving the interaction of the peroxide radicals $RO_2{}^{\cdot}$ of the substrate (strong electron acceptors) is very probable for them under the conditions of hydrocarbon oxidation. This mechanism includes the electron transfer stages:

$$>NH + RO_2{}^{\cdot} \rightarrow >NH^{\cdot +}\cdots RO_2{}^{-},$$

and then proton transfer to form ROOH and the aminyl radical $Am^{\cdot}$. A correlation between the inhibition constant k_i and the empirical characteristics of the efficiency of the inhibiting action with the oxidation potential of the amine seems quite natural in terms of this mechanism. This correlation was observed experimentally in several cases.

In the present work, we have measured potentials $E_{1/2}{}^{ox}$ of the series of HQ derivatives differing in the degree of heterocycle hydrogenation and the nature of sub-

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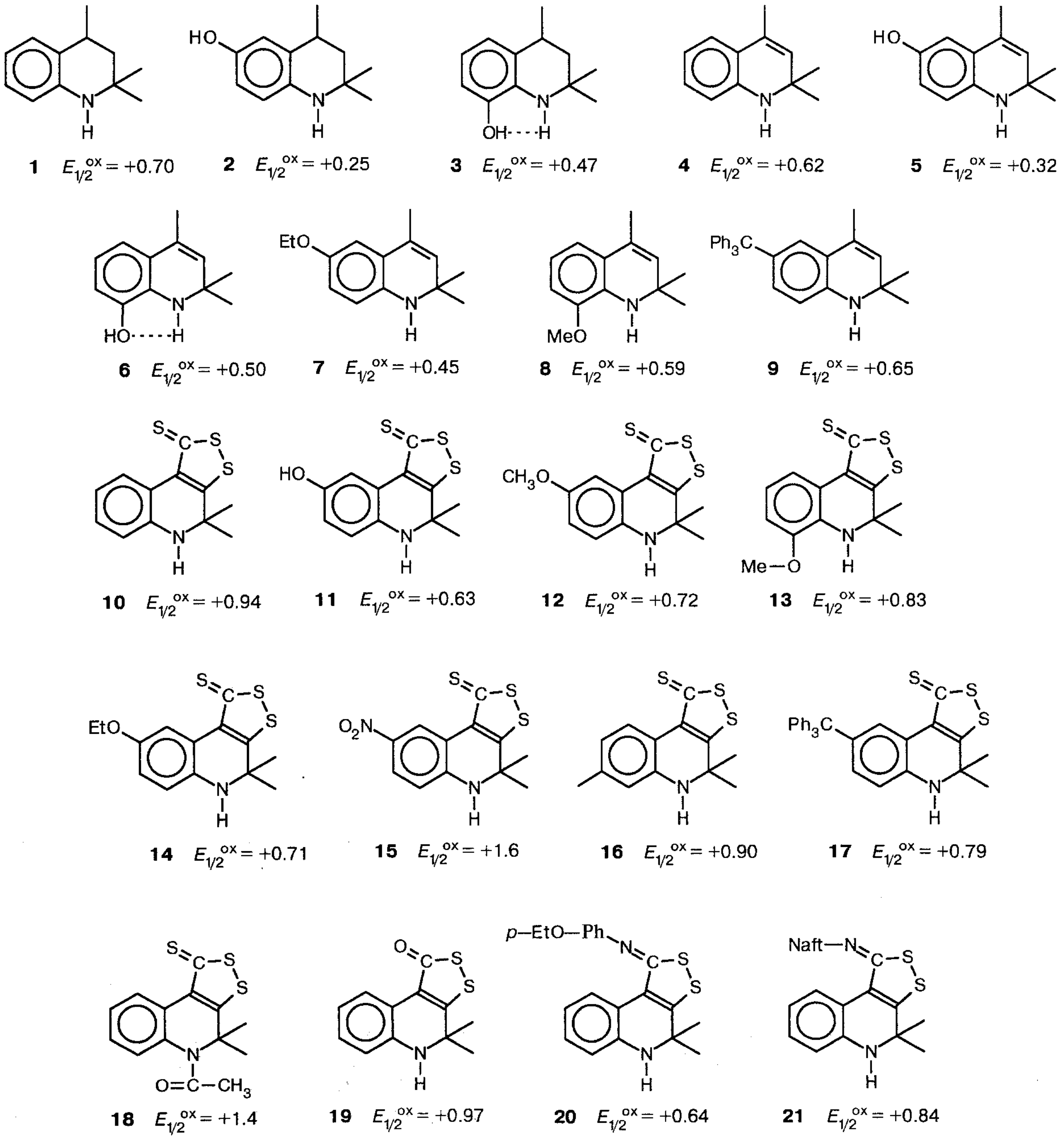
stituents in the aromatic ring and heterocycle in order to elucidate the influence of these factors on redox properties of this class of compounds and to compare electrochemical properties of HQ derivatives with their inhibiting action in the oxidation of the series of hydrocarbons.

Experimental

Tetrahydroquinolines (THQ) **1—3** and dihydroquinolines (DHQ) **4—9** were synthesized in the Institute of Chemical Physics of the Russian Academy of Sciences and IREA, and dithiolthiones (DTT) **10—21** were synthesized in the Department of Physicoorganic Chemistry of Voronezh State University[3] (Scheme 1). The purity of the compounds was checked by the TLC method.

The electrochemical oxidation of compounds **1—21** in acetonitrile was performed at 20 °C on the rotating platinum electrode of a Radelkis OH 102 polarograph. Tetraethyl-ammonium perchlorate (0.1 mol/L) was used as the supporting electrolyte, and a saturated calomel electrode served as the reference electrode. The concentration of **1—21** was $5 \cdot 10^{-4}$ mol/L. The height of the first wave of the electrochemical oxidation of the studied compounds is close to that of the one-electron oxidation wave of the standard (ferrocene) at the same concentration, which testifies to the one-electron character of the redox processes studied.

Scheme 1



1 $E_{1/2}^{ox} = +0.70$
2 $E_{1/2}^{ox} = +0.25$
3 $E_{1/2}^{ox} = +0.47$
4 $E_{1/2}^{ox} = +0.62$
5 $E_{1/2}^{ox} = +0.32$
6 $E_{1/2}^{ox} = +0.50$
7 $E_{1/2}^{ox} = +0.45$
8 $E_{1/2}^{ox} = +0.59$
9 $E_{1/2}^{ox} = +0.65$
10 $E_{1/2}^{ox} = +0.94$
11 $E_{1/2}^{ox} = +0.63$
12 $E_{1/2}^{ox} = +0.72$
13 $E_{1/2}^{ox} = +0.83$
14 $E_{1/2}^{ox} = +0.71$
15 $E_{1/2}^{ox} = +1.6$
16 $E_{1/2}^{ox} = +0.90$
17 $E_{1/2}^{ox} = +0.79$
18 $E_{1/2}^{ox} = +1.4$
19 $E_{1/2}^{ox} = +0.97$
20 $E_{1/2}^{ox} = +0.64$
21 $E_{1/2}^{ox} = +0.84$

Results and Discussion

The $E_{1/2}{}^{ox}$ values obtained for compounds **1—21** are presented in Scheme 1.

The comparison of the $E_{1/2}{}^{ox}$ values of compounds **1**, **4**, and **10**, which have no substituents in the aromatic ring, shows that the introduction of a double bond into the heterocycle facilitates oxidation, while conjugation of the heterocycle having the double bond with the dithiolthione ring makes it difficult. Substituted DTT **10—17** are oxidized at higher potentials than the corresponding DHQ **4—9**. The introduction of the dithiolthione group results in the anodic shift of $E_{1/2}{}^{ox}$ by an average of 0.3 V. This means that the sulfur atoms in the dithiolthione ring act as a strong electron acceptor. In principle, this should decrease the activity of DTT compared to that of HQ in reactions with electrophiles. The replacement of the thione sulfur atom in the dithiolthione ring with the better acceptor oxygen (**19**) somewhat increases $E_{1/2}{}^{ox}$, while its replacement with donor *N*-aryl groups (**20**, **21**) causes the opposite effect.

In the series of DHQ (**4—9**) and DTT (**10—17**) differing in the nature and the arrangement of substituents in the benzene ring, the $E_{1/2}{}^{ox}$ values correlate with those of the Hammett polar σ-constants for the *p*- and *m*-substituents (the position of the substituents is determined relative to the C(9) atom directly bound to the amino group):

$$E_{1/2}{}^{ox}(\mathrm{DHQ}) = 0.62 + 0.72\sigma, \quad (1)$$

$$E_{1/2}{}^{ox}(\mathrm{DTT}) = 0.94 + 0.87\sigma. \quad (2)$$

The comparison of Eqs. (1) and (2) shows that the degree of influence of the substituents at the aromatic ring increases somewhat as the oxidation potential of the nonsubstituted compound increases: $\rho(\mathrm{DTT}) > \rho(\mathrm{DHQ})$. A similar result is obtained for the dependences of the ionization potentials on the nature of the substituent at the ring in the series of substituted anilines ($\rho = 0.7$), toluenes ($\rho = 0.75$), benzenes ($\rho = 0.86$), and nitrobenzenes ($\rho = 0.95$).[10]

The data for compounds **9** and **17** containing the substituent $(Ph)_3C$ at the aromatic ring are of interest. In DHQ **9** this substituent acts as a weak acceptor according to the value of its polar constant ($\sigma_p = +0.08$).[11] In the presence of the dithiolthione ring in DTT molecule **17**, the same substituent acts as a donor decreasing the value of $E_{1/2}{}^{ox}$ compared to that of the nonsubstituted DTT **10** by 0.15 V. This effect is likely to be related to the intramolecular interaction of the bulky substituent with the dithiolthione cycle **17**, which results in weakening of the electron-acceptor action of the latter.

The comparison of the electrochemical properties of the HQ derivatives with the same substituents at the *p*- or *o*-positions (**2** and **3**, **5** and **6**, **7** and **8**, **12** and **13**) shows that the donor oxygen-containing substituents OH and OCH_3 at the *p*-position decrease the $E_{1/2}{}^{ox}$ value significantly more than the analogous substituents at the *o*-position. A possible reason for this may be the formation of an intramolecular O · · · H hydrogen bond with the participation of the hydrogen of the amino group in the latter case. This results in the weakening of the donor action of the substituent through the aromatic ring.

It is somewhat unexpectedly that the value of σ for the acetic group in *N*-substituted DTT **18** calculated formally from Eq. (2) and the $E_{1/2}{}^{ox}$ value is +0.52 and equals the value of the σ-constant of the acetic group. In other words, the acetic group separated from the N atom by the C_6H_4 bridge manifests the same acceptor action as that directly bound to the N atom. A similar coincidence was observed in the series of substituted carbazoles **12—14**, however, it is difficult at the present time to explain this phenomenon.

The change in $E_{1/2}{}^{ox}$ observed in the series of compounds **1—21** agrees well with some of the phenomenological peculiarities of the inhibiting action of these derivatives of HQ.[3] Active antioxidants with $k_i \geq 10^6$ l (mol s)$^{-1}$ are necessary for the inhibition of the low-temperature (50 °C) oxidation of polynonsubstituted organic compounds; therefore, considerable retardation effects are observed only in the case of hydroxy derivatives of HQ and ethoxyquine **7**.[3,4] The same compounds are characterized by the lowest values of $E_{1/2}{}^{ox}$. Dithiolthiones are inefficient as stabilizers of polyenes, however, they inhibit the oxidation of paraffins and olefins at high temperatures (150 °C) more strongly than the corresponding DHQ. Although there are several sulfur atoms in the DTT molecules, they have almost no effect on the decomposition rate of the branching agents (hydroperoxides) in these systems. Their higher stability to oxidation by molecular oxygen (the main route of the HQ consumption at elevated temperatures) seems to be a reason for the longer retardation periods in the presence of DTT. This is in accordance with the increase in $E_{1/2}{}^{ox}$ (0.63—0.94 V) compared to that of HQ. A more considerable increase in $E_{1/2}{}^{ox}$ as, e.g., in the case of nitroderivative **15** (1.6 V), results in the complete loss of the inhibiting action due to the decrease in the reactivity of the NH-group towards the chain termination.[2] In the series of DTT with different substituents at the C atom in the thione ring (**19**, **10**, and **20**), compound **20** with the lowest potential $E_{1/2}{}^{ox}$ is characterized by higher inhibiting properties in oxidizing olefins. However, in contrast to the phenolic antioxidants,[8] in the case of HQ no correlation is observed between $E_{1/2}{}^{ox}$ and the duration of the retardation periods in the oxidation of the paraffinic hydrocarbons and olefins at temperatures higher than 100°C. Obviously, this is related to the more complicated mechanism of inhibiting action of HQ, the occurrence of competitive reactions of HQ with $RO_2{}^{\cdot}$, O_2, and ROOH, and the antibatic influence of these reactions on the retardation effects.

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