REACTIONS OF N,N'-DIPHENYL-p-QUINONEDIIMINE WITH HYDROQUINONE, α-TOCOPHEROL, AND OTHER ANTIOXIDANTS

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Phenols (hydroquinone and α-tocopherol) and heterocyclic aminophenols (2,2,4-trimethyl-6-ethoxy-1,2-dihyroquinoline) reduce N,N'-diphenyl-p-quinonediimine (A) to the diamine. With difunctional hydrogen atom donors, the reaction rate is proportional to the concentrations of the reactants. The effective rate constants have been determined over a range of temperatures. In the reaction of A with α-tocopherol, plots of rate versus initial concentrations are nonlinear. 2,6-Di-tert-butyl-4-methylphenol and 2,2,4-trimethyl-6-ethoxy-1,2-dihyroquinoline do not react with A under the same conditions.

Keywords: N,N'-diphenyl-p-quinonediimine, reduction kinetics, hydroquinone, 2,2,4-trimethyl-6-ethoxy-1,2-dihyroquinoline, 2,6-di-tert-butyl-4-methylphenol (ionol), α-tocopherol, 2,2,4-trimethyl-6-ethoxy-1,2-dihyroquinoline, oxidation potentials.

Transfer of hydrogen atoms between quinonoid compounds and hydroquinones is important in many chemical [1-5] and biological [2, 6] processes. It has been shown in many cases that redox reactions such as these are responsible for the nonadditive effects of mixtures of inhibitors, including quinones or those formed during oxidation [5]. The hydrogen acceptor may also be a nitrogenous compound (a quinonimine or quinonediimine) formed by oxidation of aromatic amines or diamines [7-9]. We have not examined the kinetics of the reactions of N,N'-diphenyl-p-quinonediimine (A) with various inhibitors in order to establish the quantitative characteristics and the principal factors governing the reaction rates.

EXPERIMENTAL

Reactions of A with the inhibitors were carried out in chlorobenzene in the thermostated cell of a spectrophotometer, or in a bubbler vessel in a stream of oxygen or nitrogen. The reaction rates were independent of the type of vessel, and of the concentration of oxygen (oxygen, air, nitrogen) in solution. Consumption of A was followed spectrophotometrically by the decrease in optical density at the absorption maximum, $\lambda = 450$ nm, $\varepsilon = 6.85 \cdot 10^3$ liters/(mole·cm). The half-wave electrochemical oxidation potentials of the inhibitors were measured in a cell fitted with a rotating platinum electrode in acetonitrile solution, with tetraethylammonium perchlorate as the base electrolyte. The purity of the inhibitors used was checked by TLC.

RESULTS AND DISCUSSION

Table 1 shows the half-wave electrochemical oxidation potentials ($E^{ox}_{1/2}$) of the inhibitors (InH) used together with the literature values for the rate constant (k_H) for the removal of a hydrogen atom by peroxy radicals (usually α-phenylethylperoxy radicals at 60°C):

$$InH + RO_2^{\cdot} \rightarrow RO_2H + In^{\cdot}.$$

It will be seen that all the compounds, with the exception of ionol (3), react readily with $RO_2^{\cdot}$ ($k_H \sim 10^6$ liters/(mole·sec), but their $E^{ox}_{1/2}$ values differ considerably, the hetero-

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TABLE 1. Electrochemical and Kinetic Data for the Compounds Examined

Compound	$E_{1/2}^{ox}$, V*	k_H, liter/(mole·sec)
Hydroquinone (1)	1.05	$1.1 \cdot 10^6$ [10]
2,2,4-Trimethyl-6-hydroxy-1,2-dihydroquinoline (2)	0.32	$>1 \cdot 10^6$ [11]
2,6-Di-tert-butyl-4-methylphenol (ionol)(3)	1.3	$2.5 \cdot 10^4$ [10]
α-Tocopherol	0.78	$3.1 \cdot 10^6$ [12]
2,2,4-Trimethyl-6-ethoxy-1,2-dihydroquinoline (ethoxyquin) (5)	0.45	$1.3 \cdot 10^6$ [13]

*Relative to a saturated calomel reference electrode.

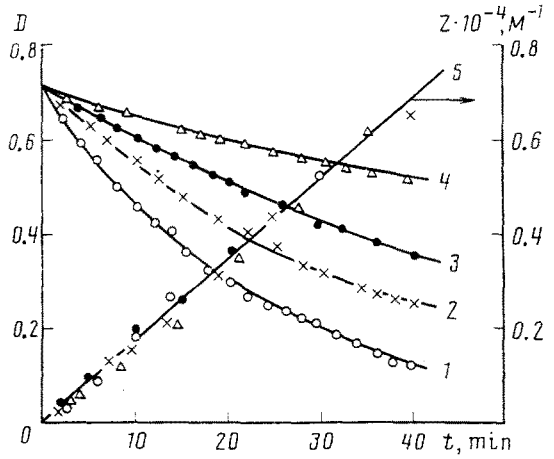


Fig. 1. Kinetic plots for the consumption of A in its reaction with (1) at 23°C. $[(1)]_0 \cdot 10^4$, M: 1) 2.4; 2) 1.8; 3) 1.2; 4) 0.6; 5) transformation of the kinetic plots in coordinates of Eq. (2).

cyclic amines (2) and (5) being oxidized much more readily than phenols (3) and (4). It might be expected that the rate of reaction of A with InH (under the same initial conditions) would increase as k_H increased and $E_{1/2}^{ox}$ decreased. No such correlation between the reaction rate and k_H or $E_{1/2}^{ox}$ was in fact found.

The reactions between A and (1) or (2), which contain two functional H-donor groups, proceed quite readily at moderate temperatures in a stoichiometric ratio of 1:1. The initial rate of consumption of A is proportional to the concentrations of the reactants

$$-d[A]/dt = k_{ef}[A][InH], \quad (1)$$

and the kinetic plots are fully linearized in the coordinates of the integral equation (2):

$$z = \frac{1}{[A]_0 - [In\,H]_0} \ln \frac{([A]_0 - x)[In\,H]_0}{([In\,H]_0 - x)[A]_0} = k_{ef}t, \quad (2)$$

where $x = [A] - [A]_0$. Typical kinetic plots and their transformations in the coordinates of Eq. (2) are shown in Fig. 1.

If, when all the A has been consumed, benzoyl peroxide (BP) is added to the reaction mixture, thereby rapidly and quantitatively oxidizing aromatic diamines to the corresponding quinonediimines [14], the optical density at the absorption maximum for A rises to its original value. This clearly indicates that in the reactions with (1) and (2) the dimine is quantitatively reduced to the diamine. Qualitative confirmation of the formation of the diamine (AH_2) was obtained by TLC.

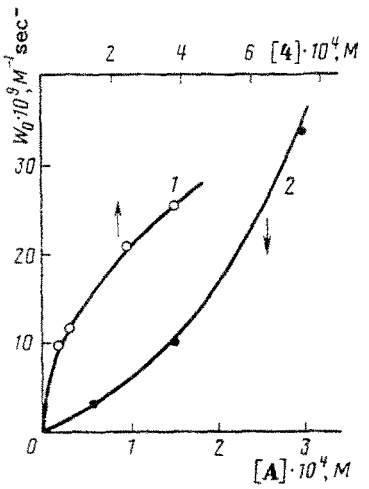
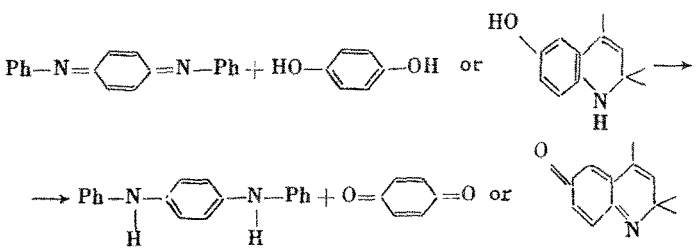


Fig. 2. Plots of the initial rate consumption of A versus the initial concentration of A (1) for $[(4)]_0 = 1.2 \cdot 10^{-3}$ M, and versus the initial concentration of (4) (2) when $[A]_0 = 1.1 \cdot 10^{-4}$ M.



The rate constants for this reaction at various temperatures (liter/(mole·sec) are shown below:

	23°	38°	49°	60°
1	2.8	–	13	–
2	5.3	16	54	190

The apparent activation energy was ∿54 kJ/mole for (1) and ∿76 kJ/mole for (2).

When ionol (3) or ethoxyquin (5) was added to A, the UV absorption spectrum remained unchanged after 3 h at 60°C, either in air or under nitrogen, i.e., these compounds do not reduce A. In the case of α-tocopherol, which has a much greater oxidation potential than (5), A is consumed. When BP is added to the reaction mixture when the reaction is complete, the optical density of the solution at the absorption maximum for A is restored to its original value, so that it may be assumed that in this case A is reduced to the diamine. The initial rate of consumption of A in its reaction with (4) (W_0) increases nonlinearly as the reactant concentrations increase (Fig. 2).

The specific rate of consumption $\bar{V} = W_0/[A]_0[(4)]_0 = 0.1\text{-}0.9$ mole/(liter·sec) is several times smaller than the value of k_{ef} for the reaction of A with (1) or (2) at lower temperatures, i.e., (4), which is oxidized and gives up a hydrogen atom more readily than hydroquinone (Table 1), is less reactive in reducing A than is (1). Comparison of the behavior of (2) and (5) in their reactions with A shows that replacement of an OH group by an ethoxy group results in a loss of reactivity in the compounds.

On the basis of the results obtained, it is clear that for the reaction A + InH to proceed, the presence of two (or more) functional H-donor groups is of great importance. The reaction is apparently facilitated by the fact that in the first step

$$A + InH = AH^{\cdot} + In^{\cdot}$$

In· and AH· radicals of the semiquinone type are formed, which rapidly disproportionate to the end products. In the case of monofunctional InH, aromatic amines may be relatively less efficient than phenols as reductants, in consequence of the high reactivity of aminyl radicals towards H atom abstraction [15].

Of particular interest is our finding that α-tocopherol can undergo redox reactions with quinoid compounds (the oxidized forms of inhibitors) of the A type. α-tocopherol (vitamin E) is a naturally occurring antioxidant which is an essential component of cell membranes. The effects and consequences of reactions of this type involving α-tocopherol should therefore be borne in mind in studies of the pharmacological properties of synthetic drugs containing quinonid groups, or forming these in the course of metabolism.

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