2. It has been found that the values of E for the solutions are close to the upper limit of the published values for the gas phase, while A exceeds the corresponding values by 1-3 orders.

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# STUDY OF DISPROPORTIONATION OF SOME SUBSTITUTED

2-HYDROXYPHENOXYL RADICALS

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Photoreduction of quinones and the reactive capacity of the hydroxyphenoxyl radicals formed have been intensively studied recently [1-9]. This is due both to finding chemically induced electronic polarization in such systems and to the presence of interesting characteristics in disproportionation reactions. Disproportionation of 4-hydroxyphenoxyl radicals thus takes place with almost diffusion-controlled rates ( $k \sim 10^8-10^9$  liter/mole·sec), and the energy barriers of this reaction are significantly lower than the activation energy of diffusion of the corresponding solvents (alcohols, ethers), A similar event has been observed in reactions of recombination of diphenylhydroxymethyl [10] and phenoxyl radicals [11]. Energy barriers of disproportionation close to zero have been observed on the example of 3,6di-tert-butyl-2-hydroxyphenoxyl (I) radicals in inert media (pentane, toluene, benzene) [12, 13], despite the fact that the rate constants of this reaction ( $\sim 10^6$  liter/mole·sec) were three orders of magnitude lower than the diffusion rate constant ( $\sim 10^9$  liter/mole·sec).

Disproportionation of sterically hindered hydroxyphenoxyl radicals was studied and the kinetic isotopic effect (KIE) was determined in the present article to reveal the generality and causes of this type of effect in disproportionation reactions (Table 1). Radicals (I)-(V) were obtained as a result of photoreduction of the initial quinones according to the scheme in [8]:

 $\begin{array}{c} \mathbf{Q} \xrightarrow{h\mathbf{v}} {}^{1}\mathbf{Q}^{*} \longrightarrow {}^{3}\mathbf{Q}^{*} \\ {}^{3}\mathbf{Q}^{*} + \mathbf{RH} \longrightarrow \dot{\mathbf{Q}}\mathbf{H} \\ 2\dot{\mathbf{Q}}\mathbf{H} \xrightarrow{k_{d}} \mathbf{Q} + \mathbf{QH}_{2} \end{array}$ 

where Q is the initial quinone; QH is the hydroxyphenoxyl radical;  $QH_2$  is the corresponding hydroquinone;  $k_d$  is the disproportionation rate constant;  $^1Q*$  is the singlet and  $^3Q*$  is the triplet excited state of the quinone.

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Radica1*	kd (H)·10−s	k <sub>d</sub> (D)•10−5	$k_{d}(H)/k_{d}(D)$	vH/vD
0· 0H				
$x - \sum_{(1)} -x$	2,2	1,5	14,5	11,0
0. HO				{
x_	6,0	4,8	12,5	
			×	
0. 0H				
X_/_CI	5,6	6,5	8,6	12,0
(III) 0. OH				
x_	5,5	2,4	23	-
(IV)				
X X				
	1,3	-	-	-
X X (V)	)			
$\star X = t - Bu$ .		1		

TABLE 1. Disproportionation Rate Constants  $(k_d)$  of 2-Hydroxyphenoxyls and Kinetic Isotropic Effect of Disproportionation and Intramolecular Migration of H and D Atoms  $(k_d, liter/mole\cdotsec)$ 

The kinetic curves of the quenching of QH radicals are described by a second-order equation, confirmed by the dependence of the steady-state concentration of photogenerated radicals on the intensity of the light to the power of 1/2.

The disproportionation rate constants for all of the radicals investigated, as in the case of protonated and deuterated analogs  $[k_d(H) \text{ and } k_d(D)]$ , were almost independent of the temperature in the -80 to -40°C range, which indicates that the effective activation energy is close to zero  $(E_a \simeq 0)$ .

Substitution of hydrogen for deuterium results in a marked decrease in  $(k_d)$ ; the KIE calculated for radicals (I)-(IV) falls within the limits of the values characteristic of reactions of radical substitution at the H(D) atom [14]. We note that the KIE of disproportionation is comparable to the KIE of intramolecular migration of the H(D) atom between the 0 atoms in radicals (I) and (III) [15-17] (see Table 1), in which there is a strong hydrogen bond (H bond) between the H atom in the OH group and the monovalent 0 atom:



It is possible to hypothesize that migration of the H(D) atom from one radical to another takes place in disproportionation reactions by formation of a radical complex (RC) with H bonds in which formation of a quinhydrone complex (QH) takes place during transfer of the hydrogen, and decomposition of this complex in turn results in the formation of quinone Q and hydroquinone QH<sub>2</sub>:



Although there is no direct evidence of the existence of RC in solutions, transfer of an H atom from QH<sub>2</sub> to Q takes place during irradiation of frozen solutions of quinone and pyrocatechol with light with formation of QH radicals. Spectra of radical pairs which in principle imitate the hypothesized RC in solution are recorded. The ESR spectra of such radical pairs are characterized by an effective spin-spin reaction of the unpaired electrons, while the radical centers are at a distance of 5-6 Å [18-20].

The kinetic scheme of disproportionation of  $\dot{Q}H$  radicals with respect to formation of an RC can be represented as follows:

$$\begin{array}{l} \mathrm{QH} + \mathrm{QH} & \xrightarrow{\sim} & \mathrm{PK} \\ \\ \mathrm{RC} & \xrightarrow{k_2} \mathrm{QH} & \rightarrow (\mathrm{Q} + \mathrm{QH}_2) \end{array}$$

(diamagnetic products)

If disproportionation takes place by formation of an RC, then the change in the concentration of radicals in time is described by the equation:

$$-\frac{d\dot{\mathbf{Q}}\mathbf{H}}{dt} = \frac{2k_2 [\text{RC}]}{1 + 4K_1 [\dot{\mathbf{Q}}\mathbf{H}]}$$

in the condition  $4K_1[\dot{Q}H] \ll 4$ , the expression assumes the form:

or

 $-\frac{d\dot{\mathbf{Q}}\mathbf{H}}{dt} = 2k_2K_1\,[\dot{\mathbf{Q}}\mathbf{H}]^2$ 

 $K_1 = [RC]/[\dot{Q}H]^2$ 

 $-\frac{d\dot{\mathbf{Q}}\mathbf{H}}{dt} = 2k_2 \left[\mathrm{RC}\right]$ 

where

This is consistent with a second-order disproportionation reaction, but the effective rate constant includes the equilibrium constant of formation of the RC (autoassociation of 
$$\hat{Q}H$$
 radicals). This process, like any formation of complexes with H bonds, is exothermic ( $\Delta H < 0$ ), and the effective activation energy of disproportionation is thus written in the form  $E_{ef} = E_d + \Delta H_1$ , where  $E_d$  is the activation barrier of disproportionation of the RC. It becomes clear that  $E_{ef} \simeq 0$  is the consequence of preliminary formation of an RC. Similar hypotheses have been advanced in [10, 11]. The same causes apparently determine the low energy barriers ( $\Im$  kcal/mole) in hydrogen exchange reactions in systems containing a phenoxyl radical and an initial phenol [21]:

 $\dot{RO} + ROH \rightleftharpoons \dot{RO}$  .....  $HOR \rightleftharpoons ROH + \dot{RO}$ 

We note that the exchange rate constants are within  $10^2-10^3$  liter/mole·sec.

The effect of formation of an intermolecular H bond in radical (I) on its reactive capacity is graphically manifested in the disproportionation reaction in appropriate solvents. For example, the  $\Delta E_{ef}$  for THF and CH<sub>3</sub>COOH are equal to 4.0 and 3.7 kcal/mole, respectively [13]. At the same time,  $\Delta H$  for complexing of radical (I) with the same solvents are -4.9 and -4.2 kcal/mole [22], and their values enter into the effective activation energy, increasing the energy barrier, since formation of an RC requires preliminary desolvation of the  $\dot{Q}H$  radicals. Inclusion of the stage of complexing of  $\dot{Q}H$  radicals by molecules of solvent (Sol)

$$\dot{\mathrm{Q}}\mathrm{H}+\mathrm{Sol} \stackrel{\mathtt{A}_{\mathtt{S}}}{\rightleftharpoons} \dot{\mathrm{Q}}\mathrm{H}_{\mathtt{Sol}}$$

where  $\dot{Q}H_{sol}$  is a solvated radical, assuming that solvated radicals disproportionate much more slowly, results in the following expression for disproportionation of  $\dot{Q}H$  radicals:

$$-\frac{d [\text{QH}]}{dt} = \frac{2k_2K_1}{K_s^2} \frac{[\text{QH}]^2}{[\text{Sol}]}; \text{ when } K_s [\text{Sol}] \gg 1$$

where  $K_{ef} = k_2 K_1 / Ks^2$  [sol]. Then  $E_{ef} = E_d - 2\Delta H_{sol} + \Delta H_1$  ( $\Delta H_{sol}$  is the heat of complexing of the QH radicals by the solvent). Hence, regardless of the value of  $E_d$  which is apparently small, we will have  $E_{ef} > 0$  for THF and  $CH_3COOH$ . It is also similar for all solvents which form an H bond with QH radicals.

 $k d^{(0^\circ)}$ <sup>k</sup>d (20°)  $\Delta H \mp 0.5$ , Kr (20°)  $K_{\Gamma}$  (0°) OH kcal/mole liter/mole • sec (I) (II) 7,6.10-6 8,5 9,7 15,2 16,8 3.3-107 \*  $1,7 \cdot 10^{-8}$ 0,280,1 0,16 107 (V) 1,0.10-11 0,84 14,8 1,3-10-6 0.13.106

TABLE 2. Thermodynamic and Kinetic Paremeters of the Equilibrium:  $Q+QH_2 \rightleftharpoons 2\dot{Q}H$ 

\*The activation energies are close to  $\Delta H$  in this case, since the effective activation energy of disproportionation is close to zero.

TABLE 3. Thermodynamic Parameters of the Equilibrium of Formation of Quinhydrone  $Q + QH_2 \stackrel{K_3}{\rightleftharpoons} (QH_2Q)^*$ 



\*The quenching coefficients of Q and (QH<sub>2</sub>Q) almost coincide.

The thermodynamics of the equilibrium

$$Q + QH_2 \rightleftarrows^{K_{\rm I}} 2QH$$

were studied for radicals (I), (II), and (V) by ESR (Table 2). The disproportionation rate constants found for these radicals permitted obtaining the kinetic parameters of the reaction of Q and  $QH_2(k-d)$ . The differences in  $K_r$  (see Table 2) reflect the role of steric hindrances and the intramolecular H bond on the value of  $K_r$ . The absence of an intramolecular hydrogen bond as a factor which increases the thermodynamic stability of 2-hydroxyphenoxyl radicals is the cause of the small values of  $K_r$  for radical (V).

Transition of the RC into a diamagnetic quinhydrone complex is assumed in the schemes of the reactions reported above. Spectrophotometric determinations of the concentration of quinhydrone were conducted to study the effect of the structure of the quinones and hydroquinones on the equilibrium constant of formation of quinhydrone:

$$Q + QH_2 \rightleftharpoons [QH_2Q]$$

The thermodynamic parameters of formation of quinhydrone are reported in Table 3. These parameters indicate the significant effect of steric factors on the value of K<sub>3</sub>.

The quinhydrone band does not appear in the electronic absorption spectra in solvating media (alcohols, ethers). Formation of a QH<sub>2</sub> H bond with these solvents impedes formation of quinhydrone.

The data obtained permit describing the energy changes which take place in transformation of quinhydrone into QH. In the equilibrium



Fig. 1. Dependence of the UV spectra of the (3,5-ditert-butyl-o-quinone + 3,5di-tert-butylpyrocatecholquinhydrone complex) system on temperature (solvent:heptane): a) 20°C (the position of the absorption line coincides with the absorption band of free o-quinone); b) -20°C; c) -50°C; d) -80°C. The absorption band was assigned to a quinhydrone complex.

 $QH_2 + Q \rightleftharpoons 2QH$ 

if  $\Delta H = 8.5$  (I) and 9.7 (II) kcal/mole, while in the equilibrium

 $QH_2 + Q \rightleftharpoons [QH_2Q]$ 

 $\Delta H = -4.3$  (I) and -7.3 (II) kcal/mole, then the values of  $-\Delta H$  of the reaction

 $[QH_2Q] \rightleftharpoons 2\dot{Q}H$ 

are equal to 12.8 and 17 kca1/mole.

The value of the pK of radical (I) is 6-7. It is obvious that the heat of autoassociation of such weak acids which result in formation of an RC is not greater than the  $\Delta H$  values indicated above.

### EXPER IMENTAL

The ESR spectra were recorded on a Varian E-12A spectrometer in evacuated ampuls. The fast reactions were studied by the method of pulsed irradiation. The kinetic curves were recorded with a stroboscopic integrator according to the method in [13]. Substitution of hydrogen for deuterium in the pyrocatechols was conducted in an  $\sim 5\%$  solution of D<sub>2</sub>O in toluene. In order to compensate for the effects due to formation of an H bond between the QD radical and D<sub>2</sub>O,  $\sim 5\%$  H<sub>2</sub>O was added to a control sample containing the same toluene solution of quinone and pyrocatechol.

The UV spectra were recorded on a Specord UV-VIS spectrometer. The temperature studies of the equilibrium  $Q + QH_2 \rightleftharpoons [QH_2Q]$  were conducted on the system described in [23].

The experimental data on measurement of the concentration of the QH complex as a function of the temperature are reported in Fig. 1. The systematic shift of the absorption band to the red side of the spectrum with a decrease in the temperature is due to a shift in the equilibrium  $QH_2 + Q \rightleftharpoons [QH_2Q]$  to the quinhydrone side.

For calculation of  $K_r$  and  $\Delta H$ , it was assumed that the equilibrium is totally shifted toward formation of a quinhydrone complex at -80°C in heptane.

<u>3-tert-Butyl-5-triphenylmethylpyrocatechol</u> (VI) and 3-tert-Butyl-5-triphenylmethyl-oquinone (VII). With heating, 1.4 g of 3-tert-butylpyrocatechol and 1.7 g of triphenylcarbinol were dissolved in 3-5 ml of m-xylene. To the reactive mixture were added 2-3 drops of concentrated  $H_2SO_4$ , and the mixture was boiled for 5-10 min. The substance separated during cooling was filtered off and washed with pentane. (VI) was obtained in the amount of 1.4 g (40%), m.p. 145-148°C (from toluene). Found: C 85.0; H 6.85%.  $C_{29}H_{28}O_2$ . Calculated: C 85.2; H 6.9%. 3-tert-Butyl-5-triphenylmethyl-o-quinone (VII) was prepared by oxidation of an alcohol solution of (VI) by HNO<sub>3</sub>, m.p. 240-242°. Found: C 85.5; H 6.6%.  $C_{29}H_{26}O_2$ . Calculated: C 85.7; H 6.4%.

#### CONCLUSIONS

1. The activation energy for disproportionation of semiquinone radicals is close to zero, while the kinetic isotopic effect is  $K_{\rm H}/k_D\approx 10$ ; a kinetic scheme which explains these mechanisms was proposed.

2. The heat of formation of a quinhydrone complex in the reaction of quinones and hydroquinones is approximately -5 kcal/mole, the heat of formation of semiquinone radicals is  $\sim 10$  kcal/mole, and the heat of formation of a quinhydrone complex from the latter is  $\sim -15$  kcal/mole.

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