Negative activation energies and compensation effects for the reactions of diarylaminyl radicals with phenols

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The temperature dependence of the rate constants of the reaction of 4,4′-disubstituted diphenylaminyl radicals (ArAr′N·) with phenols has been studied by a laser pulse photolysis technique. The linear relationships between activation energies E_1 (negative in the majority of cases) and logarithms of pre-exponential factors $\log A_1$ have been established. These results coincide with the two-parametric correlations of $\log k_1$ with σ^+ constants of substituents in phenol and aminyl radicals under isothermal conditions. The reaction rate constants decrease considerably when toluene is used instead of *n*-decane.

Key words: aminyl radicals, phenols, negative temperature coefficient, isoparametric correlations.

It has been shown previously[1,2] that the rate constants of reactions of some diarylaminyl radicals (ArAr′N·) with phenols (ArOH) decrease as the temperature increases (the negative temperature coefficient of the rate constant). This effect is known for many reactions,[3] including those involving free radicals.[4—12] However, the negative temperature effect has also been observed in nearly thermally neutral reactions of H atom transfer between reagents in non-excited states.[1,2] Even strongly exothermic reactions of alkoxyl radicals with phenols have low (not higher than the diffusion activation energies), but positive values of E_a.[13]

In the present work, the dependence of the Arrhenius parameters of the rate constant k_1 of the reaction of ArAr′N· with ArOH on the nature of substituents in the radical and phenol has been studied, and a considerable decrease in k_1 when the solvent is changed (toluene instead of *n*-decane) has been established.

Experimental

Experiments were carried out by a laser pulse photolysis technique (the third harmonics of an Nd laser, $\lambda_{exc} = 354$ nm, $\tau_{1/2} = 10$ ns, $E_\lambda = 1.3$ to 3.8 mJ).[14] Temperature-controlled quartz cells with a 1.0-cm optical length were used. Aminyl radicals ArAr′N· were generated by photoexcitation of the corresponding tetraarylhydrazines $(ArAr'N)_2$. The procedures of the synthesis and purification of the starting reagents were described in Refs. 1 and 2. Reaction rate constants k_1 were determined from the decrease in the absorption at $\lambda = 810$ nm caused by the presence of only free radicals ArAr′N·. The signal accumulation mode (10 to 30 scans) was used to increase accuracy. The results were processed on a computer attached to the pulse photolysis setup.

The reaction kinetics was studied in the 280—340 K temperature range at three or four temperatures specified with accuracy of ±0.15 K. *n*-Decane and toluene purified by the procedure similar to that described previously[15] for chlorobenzene were used as solvents. The values of σ^+ constants of substituents were used for the correlation analysis.[16]

Results and Discussion

The reactions studied can be presented as follows:

$$ArAr'N^{\cdot} + Ar''OH \xrightarrow{k_1} ArAr'NH + Ar''O^{\cdot},$$

where Ar and Ar′ are 4-XC_6H_4 and 4-YC_6H_4, respectively, and Ar″OH are nonhindered phenols 4-RC_6H_4OH and sterically hindered 2,6-di-*tert*-butyl-4-R-phenols.

The Arrhenius parameters of some reactions studied are plotted in Fig. 1. The numerical values of E_1 and $\log A_1$ are presented in Table 1. Here E_1 are the activation energies of the reactions and $\log A_1$ are the logarithms of pre-exponential factors. As can be seen from Fig. 1, each series presented has a linear dependence of E_1 on $\log A_1$. The following results were obtained in the analytic form (r are the correlation coefficients).

Series *1*. Reaction of 2,4,6-tri-*tert*-butylphenol 2,4,6-$Bu^t_3C_6H_2OH$ with radicals $Ph_2N^{\cdot}$, $(4\text{-}MeC_6H_4)_2N^{\cdot}$, and 4-$MeOC_6H_4(Ph)N^{\cdot}$ in *n*-decane (line *1*):

$$E_1 = -(66.4\pm1.5) + (10.4\pm0.3)\log A_1 \ (r = 0.9997). \quad (1)$$

Series *2*. Reaction of the $Ph_2N^{\cdot}$ radical with phenols 2,6-$Bu^t_2C_6H_3OH$, 2,6-Bu^t-4-MeC_6H_2OH,

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Table 1. Parameters of Arrhenius dependences for reactions of diarylaminyl radicals with phenols and the results of calculations of E_1 and $\log A_1$ by Eqs. (10) and (11)

Reaction	Solvent	E_1/kJ mol^{-1}		$\log(A_1$/L mol^{-1} s$^{-1})$	
		Experiment	Calculation	Experiment	Calculation
$Ph_2N^{\cdot}$ + 2,4,6-$Bu^t_3C_6H_2OH$	*n*-Decane	−9.50±1.3	−9.57	5.46±0.22	5.45
$(4\text{-}MeC_6H_4)_2N^{\cdot}$ + 2,4,6-$Bu^t_3C_6H_2OH$	*n*-Decane	−8.08±0.8	−7.74	5.59±0.14	5.63
4-$MeOC_6H_4(Ph)N^{\cdot}$ + 2,4,6-$Bu^t_3C_6H_2OH$	*n*-Decane	−6.58±1.1	−7.26	5.74±0.19	5.67
$(4\text{-}MeC_6H_4)_2N^{\cdot}$ + 4-$MeOC_6H_4OH$	*n*-Decane	−12.3±1.6	−10.3	5.63±0.28	5.81
$(4\text{-}MeC_6H_4)_2N^{\cdot}$ + 4-MeC_6H_4OH	*n*-Decane	2.67±0.59	3.04	6.98±0.07	7.01
$Ph_2N^{\cdot}$ + 2,6-Bu^t_2-4-$Bu^tOC_6H_2OH$	Toluene	−6.79±0.04	−6.68	5.95±0.03	5.98
$Ph_2N^{\cdot}$ + 2,4,6-$Bu^t_3C_6H_2OH$	Toluene	−5.70±0.81	−5.22	5.91±0.18	5.84
$Ph_2N^{\cdot}$ + 2,6-Bu^t_2-4-MeC_6H_2OH	Toluene	−5.20±1.2	−5.14	5.87±0.21	5.84
$Ph_2N^{\cdot}$ + 2,6-$Bu^t_2C_6H_3OH$	Toluene	−4.05±0.77	−3.99	5.72±0.13	5.73

2,4,6-$Bu^t_3C_6H_2OH$, and 2,6-Bu^t_2-4-$Bu^tOC_6H_2OH$ in toluene (line *II*):

$$E_1 = (57.8\pm14.2) - (10.8\pm2.4)\log A_1 \quad (r = 0.953). \qquad (2)$$

The values of E_1/kJ mol^{-1} and $\log(A_1$/L mol^{-1} s$^{-1})$ for the reaction of the $(4\text{-}MeC_6H_4)_2N^{\cdot}$ radical with sterically nonhindered phenols 4-$MeOC_6H_4OH$ and 4-MeC_6H_4OH in *n*-decane have been determined previously.[1] These data can be considered and treated as a series.

Series *3*. Reaction of $(4\text{-}MeC_6H_4)_2N^{\cdot}$ with phenols 4-RC_6H_4OH in *n*-decane

$$E_1 = -74.7 + 11.1\log A_1. \qquad (3)$$

In series *1*, the same phenol 2,4,6-$Bu^t_3C_6H_2OH$ reacts with various aminyl radicals, and in series *3*, on the contrary, the same radical $(4\text{-}MeC_6H_4)_2N^{\cdot}$ reacts with various phenols. Despite the qualitative difference in the series, each of them is characterized by an increase in E_1 as $\log A_1$ increases (compensation effect).

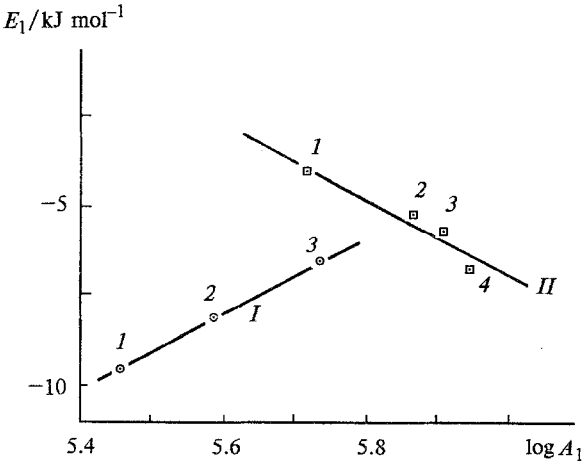

Fig. 1. Linear dependences of E_1 on $\log A_1$ in the reactions of aminyl radicals ArAr′N$^{\cdot}$ with phenols 2,6-Bu^t_2-4-R-C_6H_2OH. *I*. Reaction of 4-Me_3CArOH with various radicals in *n*-decane: $Ph_2N^{\cdot}$ (*1*), $(4\text{-}MeC_6H_4)_2N^{\cdot}$ (*2*), 4-$MeOC_6H_4(Ph)N^{\cdot}$ (*3*). *II*. Reaction of $Ph_2N^{\cdot}$ with various phenols in toluene: 2,6-$Bu^t_2C_6H_3OH$ (*1*), 2,6-Bu^t_2-4-MeC_6H_2OH (*2*), 2,4,6-$Bu^t_3C_6H_2OH$ (*3*), 2,6-Bu^t_2-4-$Bu^tOC_6H_2OH$ (*4*).

In series *2* and *3*, the ArAr′N$^{\cdot}$ radical unchanged in the series reacts with several phenols of the same type: sterically hindered in *2* and nonhindered phenols in *3*. However, the forms of correlations (2) and (3) differ, and E_1 decreases as $\log A_1$ increases in the series (reverse compensation effect). Another difference in the series considered is that in series *3* an increase in the electron-donating character of substituent R in 4-RC_6H_4OH results in the parallel decrease in E_1 and $\log A_1$, while analogous changes in the character of R in 4-R-2,6-$Bu^t_2C_6H_2OH$ result in an increase in $\log A_1$ and simultaneous decrease in E_1.

As can be seen from Fig. 1, the range of the changes in the parameters in relationships (1)—(3) presented above is not wide enough to eliminate doubts of their validity (see Ref. 3). However, convincing proof of the existence of the isokinetic dependences mentioned can be obtained from experiments at constant temperature, because the existence of linear dependences between E_1 and $\log A_1$ can cause the existence of Hammett (or analogous) correlations under isothermal conditions.

The experimental results presented in Refs. 1 and 2 (T = 294 K, *n*-decane) were used for the search of the correlations. We have restricted ourselves to the data when X, Y, and R are electron-donating groups or H atoms, because dependences (1)—(3) have been determined for these cases.

As can be seen from Fig. 2, linear dependences of $\log k_1$ (294 K) on the σ^+ constants of substituents R exist for nonhindered phenols 4-RC_6H_4OH even in the case of the $(4\text{-}BrC_6H_4)_2N^{\cdot}$ radical with electron-accepting substituents

$$\log k_1\ (294\ \text{K}) = \log k_1\ (\sigma^+_R = 0) + \rho\sigma^+_R. \qquad (4)$$

It is seen from Fig. 2, *b* that parameters $\log k_1$ ($\sigma_R{}^+ = 0$) and ρ depend, in turn, on the overall value of

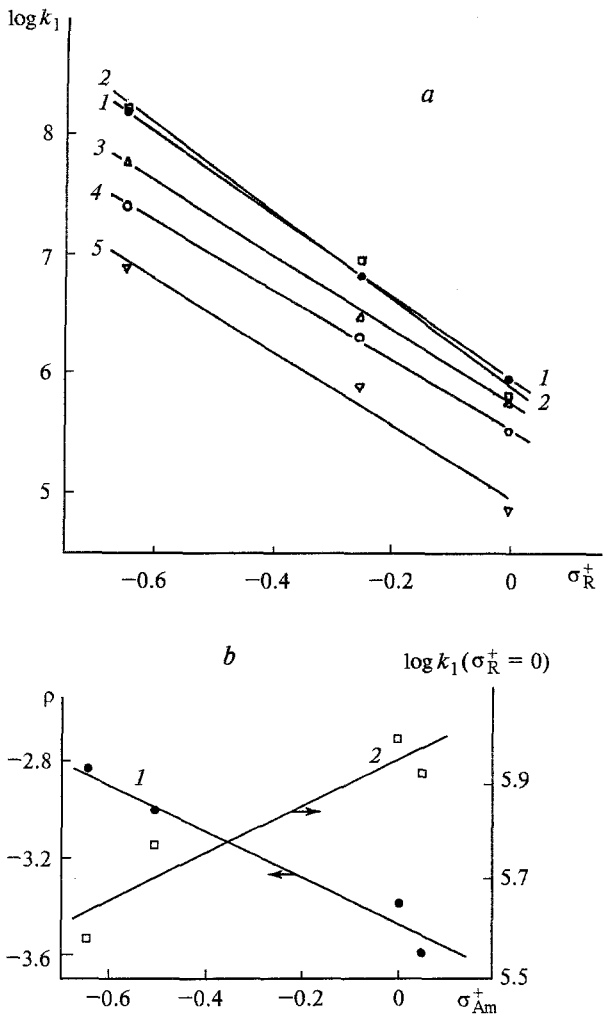

Fig. 2. *a*. Correlation between log[k_1/L mol^{-1} s^{-1} (294 K)] and σ^+ constants of substituents R in phenols 4-RC_6H_4OH for various aminyl radicals: $Ph_2N^{\cdot}$ (*1*, *5*), $(4\text{-BrC}_6H_4)_2N^{\cdot}$ (*2*), $(4\text{-MeC}_6H_4)_2N^{\cdot}$ (*3*), 4-MeOC_6H_4(Ph)N$^{\cdot}$ (*4*). Solvents: *n*-decane (*1*—*4*) and toluene (*5*). *b*. Dependences of parameters ρ (*1*) and logk_1 (σ^+_R = 0) (*2*) in Eq. (4) on σ^+ constants of substituents in radicals ArAr′N$^{\cdot}$.

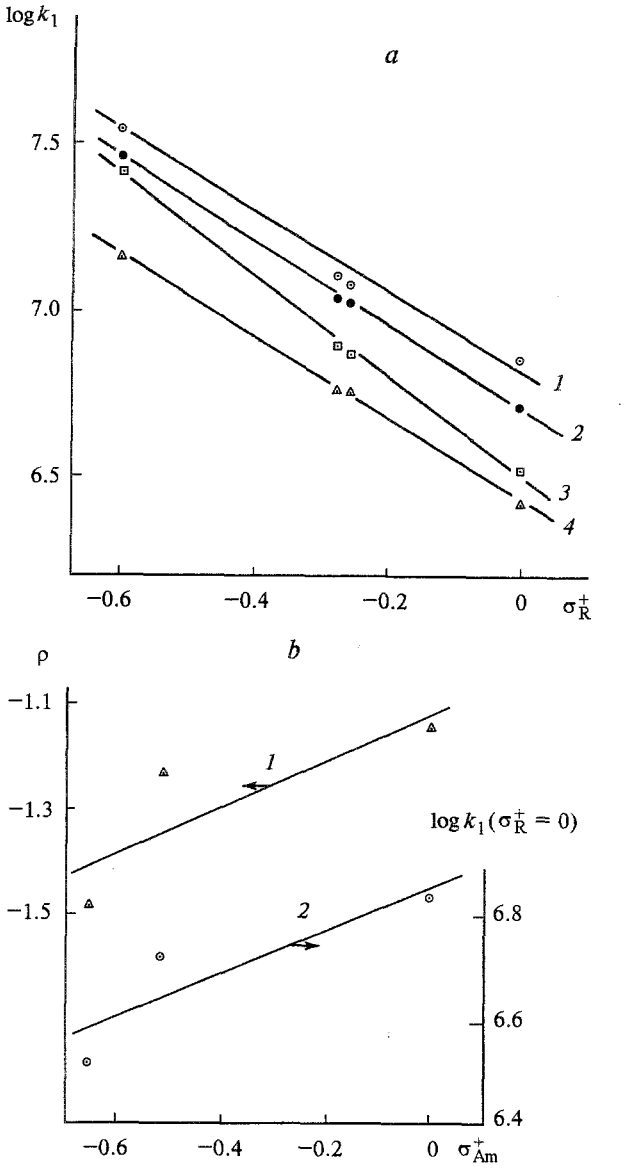

Fig. 3. *a*. Dependence of log[k_1/L mol^{-1} s^{-1} (294 K)] on σ^+ constants of substituents R in sterically hindered phenols 2,6-Bu^t_2-4-R-C_6H_2OH for various aminyl radicals: $Ph_2N^{\cdot}$ (*1*, *4*), $(4\text{-MeC}_6H_4)_2N^{\cdot}$ (*2*), 4-MeOC_6H_4(Ph)N$^{\cdot}$ (*3*). Solvents: *n*-decane (*1*—*3*) and toluene (*4*). *b*. Dependences of parameters ρ (*1*) and logk_1 (σ^+_R = 0) (*2*) in Eq. (4) on σ^+ constants of substituents in radicals ArAr′N$^{\cdot}$.

the σ^+ constants of substituents X and Y in the radicals ArAr′N$^{\cdot}$ ($\sigma_{Am}^+ = \sigma_X^+ + \sigma_Y^+$).

$$\log k_1\ (\sigma_R^+ = 0) = (5.95\pm0.05) + (0.48\pm0.13)\sigma_{Am}^+\ (r = 0.934)$$

$$\rho = -(3.47\pm0.06) - (0.93\pm0.15)\sigma_{Am}^+\ (r = 0.974)$$

Thus, one general equation can be written for lines *1*—*4* (accuracies are not presented)

$$\log k_1\ (294\ \text{K}) = (5.95\pm0.48\sigma_{Am}^+) - (3.47\pm0.93\sigma_{Am}^+)\sigma_R^+. \quad (5)$$

Line *5* in Fig. 2, *a* describes the results obtained in this work for the reaction of $Ph_2N^{\cdot}$ with 4-RC_6H_4OH in toluene at room temperature. As can be seen from Fig. 2, *a*, the aromatic solvent decreases the reaction rate constant by an order of magnitude. The parallelism of lines *1* and *5* (experiments with $Ph_2N^{\cdot}$ in *n*-decane) means that the effect is almost independent of the nature of substituent R in phenol. These results are similar to those obtained previously[17,18] for the reaction of 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) with phenols.

The dependences of logk_1 (294 K) on σ_R^+ obtained for the reactions of ArAr′N$^{\cdot}$ with sterically hindered phenols 4-RArOH are presented in Fig. 3. It is seen

from Fig. 3, *b* that the parameters of Eq. (4) linearly relate to σ_{Am}^{+} in this case as well.

$$\log k_1\ (\sigma_R^+ = 0) = (6.84\pm0.10) + (0.41\pm0.22)\sigma_{Am}^+\ (r = 0.883)$$

$$\rho = -(1.13\pm0.14) + (0.43\pm0.29)\sigma_{Am}^+\ (r = 0.832)$$

Lines *1*—*3* in Fig. 3, *a* are described by the equation

$$\log k_1\ (294\ K) = (6.84\pm0.41\sigma_{Am}^+) - (1.13 - 0.43\sigma_{Am}^+)\sigma_R^+. \quad (6)$$

Replacement of *n*-decane for toluene results in a 2—3-fold decrease in k_1, but not by an order of magnitude, as in the case of nonhindered phenols. Lines *1* and *4* in Fig. 3, *a* describing the results of the study of the reaction of $Ph_2N^{\cdot}$ with phenols 2,6-Bu^t_2-4-R-C_6H_2OH in *n*-decane and toluene are nearly parallel. Thus, as in the case of phenols 4-RC_6H_4OH, the nature of substituent R in sterically hindered phenol exerts almost no effect on the decrease in k_1 due to the replacement of the solvent. Since the numerical values of the correlation coefficients in toluene will be necessary for further discussion, let us write the equation for line *4* in Fig. 3, *a* in the form

$$\log k_1\ (294\ K) = (6.44\pm0.01) - (1.21\pm0.04)\sigma_R^+\ (r = 0.999). \quad (7)$$

Let us compare the results of isothermal experiments with the data on the temperature dependence of rate constants. Let us write correlations of one type (1)—(3) relating E_1 and $\log A_1$ in the form

$$E_1 = c + d\log A_1. \quad (8)$$

For series *2* and *3* in which the ArAr'N$^{\cdot}$ radical unchanged within the series reacts with several phenols, let us write correlations (5) and (6) in the following form (T_1 = 294 K):

$$\log k_1\ (T_1) = a_{Am} + b_{Am}\sigma_R^+. \quad (9)$$

From (8) and (9) we obtain (E_1 are expressed in kJ mol^{-1}):

$$\log k_1\ (T_1) = \log A_1 - \frac{10^3 \log e}{RT_1}(c + d\log A_1).$$

Thus, for any reaction considered, the values of E_1 and $\log A_1$ can be calculated from the correlations

$$\begin{cases} E_1 = c + d\log A_1 & (10) \\ \log A_1 = \left(a_{Am} + \dfrac{10^3 \log e}{RT_1}\cdot c + b_{Am}\sigma_R^+\right) \Big/ \left(1 - \dfrac{10^3 \log e}{RT_1}\cdot d\right). \end{cases}$$

For analysis of series *1* in which various aminyl radicals ArAr'N$^{\cdot}$ react with the same phenol, correlation (6) should be used in the form

$$\log k_1\ (T_1) = (6.84 - 1.13\sigma_R^+) + (0.41 + 0.43\sigma_R^+)\sigma_{Am}^+ = f_R + g_R\sigma_{Am}^+. \quad (6a)$$

Considerations analogous to those presented above result in the equations

$$\begin{cases} E_1 = c + d\log A_1 & (11) \\ \log A_1 = \left(f_R + \dfrac{10^3 \log e}{RT_1}\cdot c + g_R\sigma_{Am}^+\right) \Big/ \left(1 - \dfrac{10^3 \log e}{RT_1}\cdot d\right). \end{cases}$$

The values of E_1 and $\log A_1$ determined experimentally and the results of the calculations by Eqs. (10) and (11) are compared in Table 1. It can be seen that good agreement, up to coincidence, is observed in all cases. This also means that the order of the reagents arranged according to the values of parameters of dependences (1)—(3) determined on the basis of Eqs. (10) and (11) corresponds to that determined experimentally. Thus, dependences (1)—(3) are confirmed by correlations (5) and (6) and *vice versa*.

The simplest description of the reactions of aminyl radicals with phenols can be obtained in terms of the scheme

$$ArAr'N^{\cdot} + Ar''OH \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} Z \xrightarrow{k_b} Products,$$

which is usually used in similar situations due to its versatility.[3,7,13,19,20] According to this scheme, the experimentally measured parameters are the empirical characteristics of the process and are related to the parameters of the elementary stages as follows: $k_1 = K_a k_b$, $E_1 = E_a - E_{-a} + E_b = \Delta H_a + E_b$, $\log A_1 = \log A_a - \log A_{-a} + \log A_b$. When the formation of complex Z is accompanied by the heat release ($\Delta H_a < 0$) and, in addition, $|\Delta H_a| > E_b$, the experimentally measured activation energy E_1 is also negative.

The complex mechanism of the reaction of ArAr'N$^{\cdot}$ with 2,6-Bu^t_2-4-R-C_6H_2OH is the reason for the isoparametric temperature—substituent (correlations (1)—(3), isokinetic temperatures $\beta(1) = 557\pm9$ K, $\beta(2) = -587\pm126$ K, $\beta(3) = 575$ K) and substituent—substituent (correlations (5) and (6), isoparametric values $\hat{\sigma}_R^+(5) = 0.516$, $\hat{\sigma}_{Am}^+(5) = -3.73$ and $\hat{\sigma}_R^+(6) = -0.953$, $\hat{\sigma}_{Am}^+(6) = 2.63$) combinations established. Taking into account the aforesaid, we consider premature to draw any conclusions concerning the reaction mechanism on the basis of the absolute values (although very high) and the signs of the correlation coefficients in Eqs. (5) and (6).

It is likely that k_1 decreases on going from *n*-decane to toluene solvent, first of all due to complex formation of the reagents and the benzene ring of toluene (*cf.* Ref. 21). It is noteworthy that a similar value of the effect of the decrease in k on going from CCl_4 to benzene has been also established for the reactions of DPPH with phenols, and it is related[17,18] to the solvation of DPPH only. Our consideration of the reasons for the decrease in k results in the conclusion that the H-complex formation between phenol and aromatic hydrocarbon as solvent plays a considerable role in both cases. In fact, it can be obtained from the tabulated parameters of the

hydrogen bond[22] that in CCl_4 (standard solvent) equilibrium constants (K_e) of the H-complex formation between toluene and nonhindered phenols 4-RC_6H_4OH used in the work at 298 K are approximately equal, 5 L mol^{-1} ($\Delta H \approx -6.5$ kJ mol^{-1}). Under the same conditions for 2,4,6-tri-*tert*-butylphenol (and, likely, for other 2,6-Bu^t_2-4-R-C_6H_2OH phenols used), $K_e \approx$ 0.22 L mol^{-1} ($\Delta H \approx -4.5$ kJ mol^{-1}). Assuming that the replacement of CCl_4 by toluene results in only a slight change in K_e, we find that the fraction of free phenols 4-RC_6H_4OH is ~2 % in toluene, while those of 2,4,6-tri-*tert*-butylphenol and other 2,6-Bu^t_2-4-R-C_6H_2OH phenols are ~30 %. This means that if only phenols unbound in the complex with a solvent react with ArAr′N$^\cdot$, the replacement of *n*-decane by toluene as solvent would result in a decrease in k_1 of ~50-fold for 4-RC_6H_4OH and of ~3-fold for 2,6-Bu^t_2-4-R-C_6H_2OH. However, assuming that complexes of phenols with toluene are also involved in the reaction with ArAr′N$^\cdot$ with concomitant desolvation, we obtain the expected ~10-fold decrease in k_1 for 4-RC_6H_4OH and ~2.2-fold decrease for 2,6-Bu^t_2-4-R-C_6H_2OH. Despite the approximate character, the results agree well with the experiment (see above).

The above consideration allows one to assume that the H-complex formation between benzene nuclei of ArAr′N$^\cdot$ radicals and OH groups of phenols is one of the types of molecular interactions in complex Z. In addition, the ability of the nitrogen atom of aminyl radicals to accept a proton from phenol (for the information about DPPH complexes with hydrogen bonds see Refs. 23 and 24) also results in the stabilization of complexes Z formed by ArAr′N$^\cdot$ and phenols.

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