Effect of solvation on the reaction rate constants of the diphenylaminyl radical with phenols and hydroquinones

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The kinetics of the reactions of the diphenylaminyl radical with unhindered phenols and hydroquinones in acetonitrile at 294 K was studied by laser flash photolysis. The rate constants k range from 10^4 to 10^6 L mol^{-1} s^{-1} and depend on the nature of substituents in phenols and hydroquinones. The k values also depend on the solvent nature and decrease by 6.5 and 50 times, on the average, when decane is replaced by toluene and acetonitrile, respectively. The $\log k$ values in decane, toluene, and acetonitrile depend linearly on the dissociation energies D_{OH} of OH bonds in phenols and hydroquinones. Taking into account this dependence and using the experimental k value in acetonitrile, the estimate $D_{OH} = 346.6$ kJ mol^{-1} was obtained for 2,5-dichlorohydroquinone. The thermodynamic parameters of formation of H-bonded complexes of phenols and hydroquinones with toluene and acetonitrile were calculated in the framework of the multiplicative approach to thermodynamic description of H-bonding. The rate constants $k_{(free)}$ of the reactions of the diphenylaminyl radical with free phenols and hydroquinones in toluene and acetonitrile were estimated. Comparison of the $k_{(free)}$ values with each other and experimental k values in decane suggests that the changes in k upon solvent replacement is mainly caused by the formation of H-complexes of phenols and hydroquinones with the solvent.

Key words: flash photolysis, unhindered phenols, unhindered hydroquinones, diphenylaminyl radical, acetonitrile, toluene, decane, rate constants, hydrogen bond.

Phenols and aromatic amines are widely used as antioxidants.[1,2] Mixtures are frequently used instead of individual phenols and amines, because sometimes they inhibit oxidation more efficiently (synergism of the antioxidation effect of mixtures of phenols with aromatic amines).[1,3] The key role in the synergism mechanism belongs to the radical interaction of antioxidants[4] due to which the radicals of one antioxidant are replaced by the radicals of another antioxidant. Studies[5,6] of the reactions of diarylaminyl radicals with phenols in decane and toluene showed that the solvent nature exerts a substantial effect on the reaction rate; the replacement of decane by toluene decreases considerably the rate constants due to the formation of hydrogen-bonded complexes of phenols with toluene. In the present work, we continued to study the solvent effect on the reaction rate of aminyl radicals with phenols and examined the kinetics of the reactions of the diphenylaminyl radical with phenols and hydroquinones in polar aprotic solvent acetonitrile.

Experimental

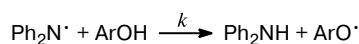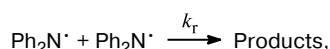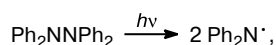A nanosecond flash photolysis technique was used.[7] The source of diphenylaminyl radicals Ph$_2$N$^\bullet$ was tetraphenyl-hydrazine Ph$_2$NNPh$_2$, which was prepared by the oxidation of diphenylamine with potassium permanganate in acetone.[8] Experiments were carried out at 294 K in a quartz cell 1.0 cm in thickness using the collinear optical scheme. Excitation of Ph$_2$NNPh$_2$ was performed by a light pulse with $\lambda_{exc} = 354$ nm (third harmonic of an Nd laser), which was inactive toward phenols and hydroquinones. Dissolved oxygen had no effect on the reaction kinetics (see also Refs 9 and 10) and, hence, experiments were carried out under aerobic conditions. Differential absorption spectra were recorded in a region of 400—1000 nm. Absorption of the diphenylaminyl radicals Ph$_2$N$^\bullet$ with the characteristic broad band with $\lambda_{max} \sim 780$ nm (see Refs 9—12) was detected immediately after a pulse (pulse duration 12 ns). The decay kinetics of the absorbance near the maximum of this band was used to determine the rate constants of the reactions of Ph$_2$N$^\bullet$ with phenols ArOH and hydroquinones Ar(OH)$_2$.

Phenols (pure grade) was purified by recrystallization first from ethanol or methanol and then (if possible according to solubility) from toluene followed by drying *in vacuo*. Unsubstituted hydroquinone was purified by recrystallization from water and methanol. Some low-melting phenols (phenol, *p*-cresol, *p*-chlorophenol) were additionally purified by recrystallization from their melt. Substituted hydroquinones were synthesized from the corresponding quinones (Aldrich) purified by double sublimation *in vacuo*. Quinones were reduced to hydroquinone with sodium dithionite using a known procedure[13] and purified by recrystallization from methanol. Aceto-
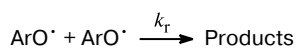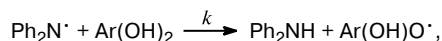
nitrile was purified and dried according to an earlier described procedure.[14]

Results and Discussion
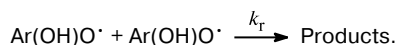
In the absence of phenols or hydroquinones, the $Ph_2N^\bullet$ radicals disappear after a flash due to recombination. Additives of ArOH or $Ar(OH)_2$ substantially accelerate the decay of $Ph_2N^\bullet$, and the curves of $Ph_2N^\bullet$ consumption become exponential beginning from rather low concentrations of ArOH or $Ar(OH)_2$. Under these conditions, the first-order rate constants k^I of $Ph_2N^\bullet$ consumption depend linearly on the concentrations of $[ArOH]_0$ or $[Ar(OH)_2]_0$ additives, indicating that after a flash the $Ph_2N^\bullet$ radicals are mainly accepted by phenol or hydroquinone, *i.e.*, $k[ArOH] \gg k_r[Ph_2N^\bullet]$ or $k[Ar(OH)_2] \gg k_r[Ph_2N^\bullet]$ (k_r is the rate constant of radical recombination)

$$Ph_2NNPh_2 \xrightarrow{h\nu} 2\,Ph_2N^\bullet,$$

$$Ph_2N^\bullet + Ph_2N^\bullet \xrightarrow{k_r} Products,$$

$$Ph_2N^\bullet + ArOH \xrightarrow{k} Ph_2NH + ArO^\bullet$$

or

$$Ph_2N^\bullet + Ar(OH)_2 \xrightarrow{k} Ph_2NH + Ar(OH)O^\bullet,$$

$$ArO^\bullet + ArO^\bullet \xrightarrow{k_r} Products$$

or

$$Ar(OH)O^\bullet + Ar(OH)O^\bullet \xrightarrow{k_r} Products.$$

The experimental rate constants of the reactions of $Ph_2N^\bullet$ with phenols were calculated by the formula

$$k = k^I/[ArOH]_0.$$

The rate constant of the reaction of $Ph_2N^\bullet$ with hydroquinones (based on one OH group) was calculated by the equation

$$k = k^I/2[Ar(OH)_2]_0,$$

where k^I is the experimental first-order rate constant of $Ph_2N^\bullet$ decay; $[ArOH]_0$ and $[Ar(OH)_2]_0$ are the analytical concentrations of phenol and hydroquinone, respectively.

The results of studying the reactions of $Ph_2N^\bullet$ with ArOH and $Ar(OH)_2$ are presented in Table 1 along with the presently recommended dissociation energies of the O—H bond in phenols D_{OH}. The D_{OH} values in Table 1 differ from those used earlier[5,6] for the reactions of $Ph_2N^\bullet$ with ArOH in decane and toluene. Therefore, the earlier obtained[5,6] k values are also given in Table 1 for a more correct comparison of k in different solvents.

The data in Table 1 show that k depends strongly on the solvent nature. The k values in toluene are by almost an order of magnitude lower than those in n-decane, while those in acetonitrile are by almost an order of magnitude lower than the k values in toluene. The solvent effect on the dependence of $\log k$ on the dissociation energy of the OH bond in phenols and hydroquinones is shown in Fig. 1. It is seen that a linear dependence between $\log k$ and D_{OH} is fulfilled in all the three solvents. Based on the data in Table 1 for seven reactions of $Ph_2N^\bullet$ with phenols, we

Table 1. Rate constants k^a of the reactions of the diphenylaminyl radical $Ph_2N^\bullet$ with phenols and hydroquinones in n-decane, toluene, and acetonitrile at 294 K obtained in Refs 5 and 6 and the dissociation energies of the O—H bond in the phenols and hydroquinones D_{OH} (kJ mol^{-1})

Phenol or hydroquinone	$k \cdot 10^{-6}$/L mol^{-1} s^{-1}			D_{OH}/kJ mol^{-1}	References
	n-Decane	Toluene	Acetonitrile		
C_6H_5OH	0.98	0.075	0.00877	369.2	15, 16
$4\text{-}ClC_6H_4OH$	2.9	0.71	0.118	366.4	16, 17
$4\text{-}MeC_6H_4OH$	7.00	0.83	0.231	360.2	16, 17
$4\text{-}MeOC_6H_4OH$	150	7.8	1.13	345.6	16, 17
$4\text{-}Me_3COC_6H_4OH$	—	—	1.28	347.8	18
$2,6\text{-}Me_2C_6H_3OH$	21.1	6.0	—	355.3	15, 16
$2,4,6\text{-}Me_3C_6H_2OH$	50.0	—	—	345.9	15, 16
$2,6\text{-}(MeO)_2C_6H_3OH$	29.2	—	—	350.0	15, 16
$4\text{-}HOC_6H_4OH$	—	—	$0.665^{\,c}$	352	18
$2,5\text{-}(Me_3C)_2\text{-}4\text{-}HOC_6H_2OH$	$262^{\,c}$	—	$4.87^{\,c}$	$(339.5)^b$	—
$2,5\text{-}Me_2\text{-}4\text{-}HOC_6H_2OH$	—	—	$4.16^{\,c}$	$(340.3)^b$	—
α-Tocopherol	—	300	—	330.3	19
$2,5\text{-}Cl_2\text{-}4\text{-}HOC_6H_2OH$	—	—	$1.45^{\,c}$	$(346.6)^b$	—

^{a} The average error is $\pm 10\%$.

^{b} Obtained in the present work, see text.
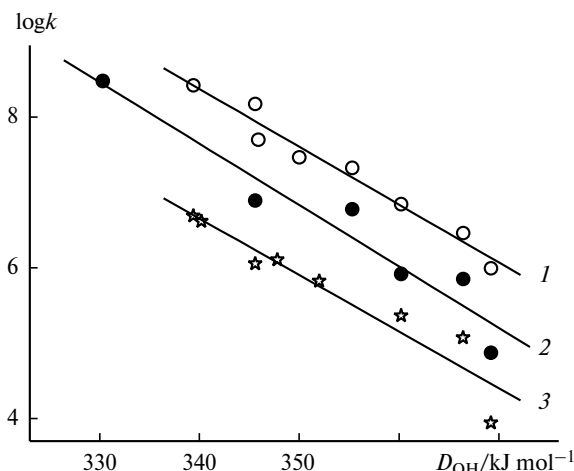
^{c} Calculated per one OH group.

Fig. 1. Solvent effect plotted as $\log k$ *vs.* dissociation energy of the OH bond in the phenols and hydroquinones: *n*-decane (*1*), toluene (*2*), and acetonitrile (*3*).

can write that this dependence in decane is described by the equation

$$\log k \ [\text{L mol}^{-1}\text{ s}^{-1}] =$$
$$= (34.46\pm2.8) - (7.67\pm0.79)\cdot 10^{-2}\cdot D_{\text{OH}} \text{ kJ mol}^{-1}. \quad (1)$$

The D_{OH} value in 2,5-di-*tert*-butylhydroquinone can be estimated using Eq. (1). Taking into account that $k = 2.6\cdot 10^8$ L mol^{-1} s^{-1} per one OH group (see Table 1), we obtain $D_{\text{OH}} = 339.5$ kJmol^{-1}. This estimate differs from the earlier found $D_{\text{OH}} = 345.4$ kJ mol^{-1},[5] but is closer to the later data $D_{\text{OH}} = 337.3$ kJ mol^{-1} (see Ref. 20). It should be mentioned that the difference between the value determined in the present work and the earlier[5,20] estimates of D_{OH} for 2,5-di-*tert*-butylhydroquinone is caused only by different sets of refined D_{OH} values in ArOH for processing the same experimental data from the rate constants of the reactions of Ph$_2$N$^\bullet$ with phenols in decane (see Eq. (1)).

Using the D_{OH} values presented in Table 1 and experimental data on the rate constants of the reactions of Ph$_2$N$^\bullet$ with six phenols in toluene, we obtain for the reactions in this solvent

$$\log k \ [\text{L mol}^{-1}\text{ s}^{-1}] =$$
$$= (35.4\pm3.9) - (8.15\pm1.11)\cdot 10^{-2}\cdot D_{\text{OH}} \text{ kJ mol}^{-1}. \quad (2)$$

To obtain a similar dependence for the reactions in acetonitrile, we used the data on the k values of the reactions of Ph$_2$N$^\bullet$ with five phenols and three hydroquinones, *viz.*, unsubstituted hydroquinone, 2,5-di-*tert*-butylhydroquinone, and 2,5-dimethylhydroquinone. For 2,5-di-*tert*-butylhydroquinone we used the above value $D_{\text{OH}} = 339.5$ kJ mol^{-1}, and $D_{\text{OH}} = 340.3$ kJ mol^{-1} was used for 2,5-dimethylhydroquinone. The latter was obtained with account for published data,[21] according to which D_{OH} in

2,5-dimethylhydroquinone is by 0.8 kJ mol^{-1} higher than D_{OH} in 2,5-di-*tert*-butylhydroquinone. Processing of the experimental data for the reactions in acetonitrile (see Table 1) gives

$$\log k \ [\text{L mol}^{-1}\text{ s}^{-1}] =$$
$$= (32.16\pm3.4) - (7.50\pm0.96)\cdot 10^{-2}\cdot D_{\text{OH}} \text{ kJ mol}^{-1}. \quad (3)$$

Equations (1)—(3) can be written in the general form

$$\log k = a + b D_{\text{OH}}.$$

Figure 1 shows that straight lines *1—3* are virtually parallel. This implies that $b \approx$ const and the solvent nature affects mainly the value of the *a* parameter.

Equations (1)—(3) show that the *a* and *b* parameters have high relative errors. This is caused by inaccuracy of experimental measurements and also a narrow range of changing D_{OH} in phenols and hydroquinones (~30 kJ mol^{-1} in the interval from 340 to 370 kJ mol^{-1}). Low accuracy of the numerical *a* and *b* values does not allow direct use of them to be performed for making conclusions about the solvent effect on *k*.

Since lines *1—3* in Fig. 1 are parallel, we decided that quite reliable conclusions can be drawn from comparison of the $\log k$ values in different solvents at the averaged D_{OH} value. For this purpose, we used formulas (1)—(3) (ignoring errors) to calculate the $\log k$ values in decane, toluene, and acetonitrile at $D_{\text{OH}} = 355$ kJ mol^{-1} taken as the average D_{OH} value in phenols and hydroquinones in Fig. 1:

Solvent	$\log k^a$	$\Delta\log k^b$
n-Decane	7.22	—
Toluene	6.40	0.82
Acetonitrile	5.53	1.69

[a] At $D_{\text{OH}} = 355$ kJ mol^{-1}. [b] $\Delta\log k = \log k_{(\text{decane})} - \log k_{(\text{solv})}$.

These data show that the *k* rate constants of the reaction of Ph$_2$N$^\bullet$ with ArOH in toluene are, on the average, by 0.8 orders of magnitude (by 6.5 times) lower than those for the reaction in decane, whereas in acetonitrile they are by 1.7 orders of magnitude (by 50 times) lower than those for the reaction in decane.

The main reason for differences in the experimental *k* values in decane, toluene, and acetonitrile is a hydrogen bond of ArOH and Ar(OH)$_2$ with solvents Solv (toluene and acetonitrile). Only molecules unbounded into an H-complex react,[22—25] which is shown in the following reaction scheme:

$$\text{ArOH}_{\text{free}} + \text{Solv} \underset{}{\overset{K}{\rightleftharpoons}} [\text{ArOH}...\text{Solv}],$$

$$\text{Ph}_2\text{N}^\bullet + \text{ArOH}_{\text{free}} \xrightarrow{k_{(\text{free})}} \text{Ph}_2\text{NH} + \text{ArO}^\bullet,$$

$$\text{Ph}_2\text{N}^\bullet + [\text{ArOH ... Solv}] \xrightarrow{\times} .$$
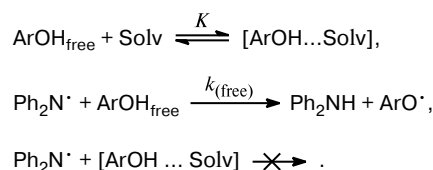
Table 2. Enthalpy (E_d) and free-energy (C_d) factors of the phenols and hydroquinones[26,30] calculated in the framework of the multiplicative approach to thermodynamic description of H-bonding, enthalpies ΔH (kJ mol^{-1}), free energies ΔG (kJ mol^{-1}) of formation of H-complexes of the phenols and hydroquinones with the solvents, equilibrium constants of formation of H-complexes with the solvents K_{294}, and the rate constants of the reactions of Ph$_2$N$^\bullet$ with free phenol and hydroquinone molecules $k_{(free)}$

Phenol or hydroquinone	$-E_d$	$-C_d$	$-\Delta H$		$-\Delta G$		K_{294} /L mol^{-1}		$k_{(free)} \cdot 10^{-6}$ /L mol^{-1} s^{-1}	
	(kJ mol^{-1})$^{1/2}$		I[a]	II[b]	I[a]	II[b]	I[a]	II[b]	I[a]	II[b]
C$_6$H$_5$OH	2.50	2.50	6.45	17.36	4.02	4.81	5.18	7.16	3.73	1.20
4-ClC$_6$H$_4$OH	2.65	2.81	6.83	18.40	5.23	6.11	8.50	12.2	57.5	27.3
4-MeC$_6$H$_4$OH	2.36	2.40	6.09	16.39	3.63	4.39	4.42	6.03	35.3	26.6
4-MeOC$_6$H$_4$OH	2.43	2.41	6.27	16.87	3.67	4.43	4.49	6.13	337	132
4-Me$_3$COC$_6$H$_4$OH	—	—	—	—	—	—	—	—	—	—
2,6-Me$_2$C$_6$H$_3$OH	1.60	1.72	4.13	—	0.99	—	1.50	—	84.7	—
2,4,6-Me$_3$C$_6$H$_2$OH	—	—	—	—	—	—	—	—	—	—
2,6-(MeO)$_2$C$_6$H$_3$OH	—	—	—	—	—	—	—	—	—	—
4-HOC$_6$H$_4$OH	2.41	2.38	6.22	16.74	3.55	4.31	4.27	5.83	—	74.1
2,5-(Me$_3$C)$_2$-4-HOC$_6$H$_2$OH	2.52	2.21	6.50	17.50	2.89	3.59	3.26	4.34	—	405
2,5-Me$_2$-4-HOC$_6$H$_2$OH	2.48	2.20	6.40	17.22	2.85	3.55	3.21	4.27	—	341
α-Tocopherol	—	—	—	—	—	—	—	—	—	—
2,5-Cl$_2$-4-HOC$_6$H$_2$OH	2.60	2.44	6.71	18.05	3.79	4.56	4.71	6.46	—	179

[a] Toluene.

[b] Acetonitrile.

We estimated the enthalpies ΔH and free energies ΔG of H-complex formation of the phenols and hydroquinones with toluene and acetonitrile in the framework of the multiplicative approach* to thermodynamic description of H-bonding[26] and, based on these data, obtained estimates for the complex formation constants K and rate constants $k_{(free)}$ of the reactions of Ph$_2$N$^\bullet$ with nonassociated ArOH and Ar(OH)$_2$ molecules. According to this method, ΔH and ΔG were calculated by the formulas

$$\Delta H \text{ (kJ mol}^{-1}) = 4.96 E_a E_d,$$

$$\Delta G \text{ (kJ mol}^{-1}) = -RT\ln K = 2.43 C_a C_d + 5.7,$$

where E and C are the enthalpy and free-energy factors of the H-acceptor (a) (solvent) and H-donor (d) (phenol or hydroquinone), respectively. The E and C factors characterize the relative ability to form an H-bond relative to standard substances: unsubstituted phenol ($E_d = -2.50$, $C_d = -2.50$) and hexamethylphosphorotriamide ($E_a = 2.50$, $C_a = 4.00$). The E and C values (in (kJ mol^{-1})$^{1/2}$) for other compounds determined from experimental data are tabulated and published.[26,30] For decane $E_a \approx 0$ and $C_a \approx 0$, for toluene[26] $E_a = 0.52$ and $C_a = 1.60$, and for acetonitrile[30] $E_a = 1.40$ and $C_a = 1.73$ (kJ mol^{-1})$^{1/2}$.

The $k_{(free)}$ value was calculated by the formula

$$k_{(free)} = k(1 + K[\text{Solv}])$$

using the experimental k values and calculated K values. For toluene and acetonitrile [Solv] = 9.41 and 18.9 mol L^{-1}, respectively.

The results obtained are given in Table 2. These data should be considered as tentative, because they were obtained under some assumptions.* The data in Tables 1 and 2 show that for the phenols and hydroquinones under study the calculated $k_{(free)}$ values in toluene and acetonitrile exceed the experimental k values in decane by at most an order of magnitude, and the $k_{(free)}$ values in toluene is by at most 2—3 times higher than $k_{(free)}$ in aceto-

* Several approaches were proposed, see Refs 26—29.

* Calculations of ΔH were performed for standard (in the multiplicative approach) conditions[26]: temperature 298 K, solvent CCl$_4$, complex composition H-donor (phenol)—H-acceptor (solvent) (1 : 1). In calculations we thus accepted that (1) composition of the phenol—solvent complex (1 : 1) is independent of the solvent concentration and (2) complexation rate constant is independent of the solvent composition (or, which is the same, on the activity coefficients γ of the substances involved in equilibrium in decane, toluene, and acetonitrile, which are equal to each other and to the γ value in CCl$_4$). The problem of applicability and precision of these approximations was discussed for the first time for the reactions of phenols (and *tert*-butyl hydroperoxide) with cumyloxyl radicals.[25,31] Later these approximations were used to interpret the data on the kinetics of the reactions of phenols with the 1,1´-diphenyl-2-picrylhydrazyl,[32,33] cumylperoxyl,[34] and alkyl[35] radicals.

nitrile. This scale of differences in $k_{\text{(free)}}$ is compared with the inaccuracy of calculations caused by differences in the activity coefficients of the components of equilibrium of ArOH and Ar(OH)$_2$ with the solvents and the reactions of Ph$_2$N$^{\bullet}$ with ArOH and Ar(OH)$_2$ in CCl$_4$, toluene, acetonitrile, and decane.[31] Based on the obtained data, we can conclude that the experimental rate constants of the reactions of Ph$_2$N$^{\bullet}$ with ArOH and Ar(OH)$_2$ in toluene and acetonitrile are lower than those in decane due to the formation of H-complexes of the solvents (toluene and acetonitrile) with ArOH and Ar(OH)$_2$ molecules. This assumption has been advanced earlier[5,6] and agrees with the data on the effect of the solvent nature on the rate constants of the reactions of phenols with other free radicals.[25,31−37]

The linear dependence (3) between log$k$ and D_{OH} in acetonitrile was used to estimate D_{OH} in 2,5-dichloro-hydroquinone for which the respective data are lacking. Substituting $k = 1.45 \cdot 10^6$ L mol^{-1} s^{-1} into (3), we obtain D_{OH}(2,5-Cl$_2$-4-HOC$_6$H$_2$OH) = 346.6 kJ mol^{-1}. This value is by 5.4 kJ mol^{-1} lower than D_{OH} in unsubstituted hydroquinone, which is somewhat unexpected, because the electron-withdrawing substituents usually increase D_{OH} in the phenols and hydroquinones and the electron-releasing substituents decrease D_{OH} (see Refs 16,18, and 38).

Thus, it follows from the obtained data that the diphenylaminyl radicals are highly reactive in the reaction of H abstraction from phenols and hydroquinones; the k rate constant depends on the nature of substituents in phenols and hydroquinones and on the solvent nature. The k values in decane at 294 K lie in a range of 10^6—10^8 L mol^{-1} s^{-1} and decrease by 6.5 and 50 times, on the average, when decane is replaced by toluene and acetonitrile, respectively. The dependence of k on the solvent nature is caused by the formation of H-complexes of the phenols and hydroquinones with the solvent. The logarithms of the rate constants log$k$ for the reactions in decane, toluene, and acetonitrile depend linearly on the dissociation of the O—H bonds in the phenols and hydroquinones. Using this dependence and the rate constant of the reaction of Ph$_2$N$^{\bullet}$ with 2,5-dichlorohydroquinone in acetonitrile, we estimated the dissociation energy of the O—H bond in 2,5-dichlorohydroquinone $D_{\text{OH}} = 346.6$ kJ mol^{-1}.

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