Kinetics of the interaction of ketyl and semiquinone radicals with dioxygen. Concerted electron and proton transfer involving ketyl and semiquinone radicals

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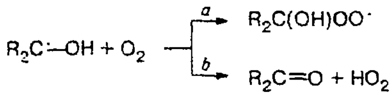
Kinetics of the interaction of ketyl and neutral semiquinone radicals with dioxygen was studied by the flash photolysis technique. The reactivity of neutral semiquinone radicals in the transfer of a hydrogen atom to O_2 is lower than that of ketyl radicals and increases as the reduction ability of the radicals increases, which gives evidence for the charge transfer from the radicals to O_2 in the transition state of the reaction. The deuterium kinetic isotope effect of the reaction (up to 2.6) suggests considerable weakening of the O—H bond of the semiquinone radical in the transition state. A cyclic structure of the transition state similar to that in the reactions of ketyl radicals with hydrogen atom acceptors is proposed. In aprotic solvents, solvation has essentially no effect on the reactivity of neutral anthrasemiquinone radicals up to solvent nucleophilicity $B \approx 240$. In solvents with higher nucleophilicity and in protic solvents, their reactivity drops sharply. Hydrogen atom transfer reactions involving ketyl and neutral semiquinone radicals are shown to involve concerted electron and proton transfers, and to have transition states in which the partial transfer of an electron and a proton from the ketyl or semiquinone radical to an acceptor occurs.

Key words: flash photolysis, ketyl and semiquinone radicals, interaction with dioxygen; concerted electron—proton transfer.

The oxidation of alcohols by molecular oxygen occurs with the formation of ketyl and semiquinone radicals;[1] however, the interaction of these intermediates with dioxygen has been poorly studied. Ketyl radicals ($R_2C^{\cdot}$—OH) are known to react with dioxygen to form addition products (the corresponding peroxide radicals) or to react by H atom transfer with regeneration of the initial ketone:[2–8]



$$R_2C^{\cdot}{-}OH + O_2 \begin{cases} \xrightarrow{a} R_2C(OH)OO^{\cdot} \\ \xrightarrow{b} R_2C{=}O + HO_2^{\cdot} \end{cases} \qquad (1)$$

In the opinion of a number of authors,[2,5–8] the reaction of H atom transfer (path *b*) is more plausible for ketyl radicals than the addition reaction (path *a*). The rate constants for the interaction of ketyl radicals of benzophenone, acetophenone, and xanthone with dioxygen in benzene were found to be $(2.3\pm0.3)\cdot10^9$, $\sim3\cdot10^9$, and $(2.8\pm0.5)\cdot10^9$ mol L^{-1} s^{-1}, respectively.[2,8] Among semiquinone radicals, only the reactivity of quinone radical anions $Q^{\cdot-}$ toward dioxygen has been studied. It was shown that,[9] whereas the radical anions of anthraquinone (AQ) efficiently react with dioxygen according to the reaction

$$AQ^{\cdot-} + O_2 \rightarrow AQ + O_2^{\cdot-}\ (k = 5\cdot10^8 \text{ mol L}^{-1}\text{ s}^{-1}), \qquad (2)$$

the radical anions of benzoquinone (BQ) essentially do not react with dioxygen, and the reverse reaction occurs:

$$BQ + O_2^{\cdot-} \rightarrow BQ^{\cdot-} + O_2\ (k = 1.0\cdot10^9 \text{ mol L}^{-1}\text{ s}^{-1}). \qquad (3)$$

The reactivity of neutral semiquinone radicals $QH^{\cdot}$ toward dioxygen has not been much investigated.

In the present work, the interaction of neutral semiquinone ($QH^{\cdot}$) and ketyl ($R_2C^{\cdot}$—OH) radicals with dioxygen was studied in different solvents:

$$QH^{\cdot} + O_2 \xrightarrow{k_H} \text{Products}, \qquad (4)$$

$$Ar_2C^{\cdot}{-}OH + O_2 \xrightarrow{k_H} \text{Products}. \qquad (5)$$

The semiquinone radicals of 1,4-benzoquinone, tetramethyl-1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone and the ketyl radicals of 4,4′-substituted benzophenones were used for determining the rate constants (k_H) of these reactions.

Experimental

To obtain semiquinone and ketyl radicals, we used the triplet quinone (Q) or ketone ($R_2C{=}O$) reactions of H atom

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abstraction from a solvent (or from hydrogen donor additives, 2,4,6-trimethylphenol or isopropyl alcohol):

$$Q(S_0) + h\nu \rightarrow Q(S_1) \rightarrow Q(T), \tag{6}$$

$$Q(T) + MH \rightarrow QH^{\cdot} + M^{\cdot}, \tag{7}$$

$$R_2C{=}O(S_0) + h\nu \rightarrow R_2C{=}O(S_1) \rightarrow R_2C{=}O(T), \tag{8}$$

$$R_2C{=}O(T) + MH \rightarrow R_2C^{\cdot}{-}OH + M^{\cdot}, \tag{9}$$

where MH is the solvent or the additive.

1,4-Benzoquinone, tetramethyl-1,4-benzoquinone (duroquinone), 1,4-naphthoquinone, and 9,10-anthraquinone were used as the quinones, and benzophenone and its derivatives (4-bromobenzophenone, 4,4′-dimethylbenzophenone, and 4-benzoylbenzoic acid) were the ketones. The concentration of quinones or ketones in solutions was $\sim 10^{-4}$ mol L^{-1}, the concentration of the ketyl or semiquinone radicals formed by photoexcitation was $\sim 10^{-6}$ mol L^{-1}. To increase the yield of neutral radicals when working with quinones in polar solvents, we added 10^{-2} mol L^{-1} H_2SO_4 to the solutions, because neutral semiquinone radicals, unlike ketyl radicals, are characterized by rather low pK values for the equilibrium

$$QH^{\cdot} \xrightleftharpoons{K} Q^{\cdot -} + H^{+}. \tag{10}$$

Whereas for the benzophenone ketyl radical in aqueous solutions pK = 9.2,[10] for the semiquinone radicals of 1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone pK = 4.0, 4.1, and 5.3, respectively.[11] The addition of H_2SO_4 has essentially no effect on the k_H values. In the reaction of the anthrasemiquinone radical with O_2 in different solvents, the addition of isopropanol (1—5%) to the solvents (except for toluene) also has essentially no effect on k_H. 2,4,6-Trimethylphenol was purified by sublimation and recrystallization. "Pure" grade dioxane, ethyl acetate, chloroform, pentanol, 3-methyl-1-butanol, methanol, acetonitrile, dimethylformamide, dimethyl sulfoxide, "chemically pure" grade toluene, benzene ("for UV spectroscopy" grade), "extra pure" grade isopropyl alcohol, and distilled water were used as solvents. Dioxane, ethyl acetate, dimethylformamide, pentanol, 3-methyl-1-butanol, chloroform, and methanol were purified by distillation; acetonitrile was purified by refluxing successively over NaH, P_2O_5, and CaH_2 followed by slow rectification on a 1.5 m column. The rate constants of the reactions, k_H, were determined by flash photolysis on an apparatus with a flash energy of 50 J and duration (at the half height) of 7 μs, using the decay kinetics of ketyl and semiquinone radicals observed at wavelengths close to the absorption maxima of the radicals (415, 370, and 375 nm for the neutral semiquinone radicals of 1,4-benzoquinone, 1,4-naphthoquinone, and 9,10-anthraquinone, respectively,[11] and 550 nm for the ketyl radicals of substituted benzophenones[12]), with regard to the data on the solubility of oxygen in different solvents[13,14] when saturating the solutions with air and oxygen at atmospheric pressure. The solubility of O_2 in toluene, dioxane, dimethyl sulfoxide, pentanol, 3-methyl-1-butanol, as well as in water with 14% isopropyl alcohol was determined using a manometric apparatus. The same apparatus was used to obtain intermediate concentrations of oxygen in solutions.

Results and Discussion

The rate constants of reaction (5), k_H, for ketyl radicals of substituted benzophenones are presented in Table 1. It can be seen that the k_H values are in the range of $(1.5–4.2) \cdot 10^9$ mol L^{-1} s^{-1} (for the ketyl radical of unsubstituted benzophenone in toluene k_H = $3.6 \cdot 10^9$ mol L^{-1} s^{-1}, which is close to the value presented in the literature[2]) and are little affected by variation of the nature of the substituents in the benzophenone ketyl radicals or by variation of the solvent. The large values of k_H (in particular, the values of k_H in isopropyl alcohol are close to the diffusion limit $5 \cdot 10^9$ mol L^{-1} s^{-1} estimated from Debye's formula) show that dioxygen is highly reactive toward ketyl radicals. This fact probably equalizes the k_H values for different ketyl radicals in different solvents. A similar reaction of H atom transfer from ketyl radicals occurs if azomethine dyes (AD) (pyrazolone, indoaniline, and benzoylacetanilide dyes)[15] or nitroxyl radicals (4-substituted 2,2,6,6-tetramethylpiperidine-1-oxyls)[16] rather than O_2 are used as hydrogen acceptors. The k_H values for the corresponding reactions of these compounds are well below the diffusion limit. This is due to the fact that the reactivities of the azomethine dyes and nitroxyl radicals studied are lower than that of dioxygen.

Table 1. The k_H values for the reaction of ketyl radicals of 4,4′-substituted benzophenones with dioxygen in different solvents

Solvent	$k_H \cdot 10^9$/mol L^{-1} s^{-1}			
	COOH, H	Br, H	H, H	Me, Me
Toluene*	—	4.1	3.6	4.2
Dioxane	1.5	1.6	1.5	1.8
Chloroform	1.9	—	1.9	2.2
Acetonitrile	3.3	4.0	3.3	3.6
Dimethylformamide*	—	2.1	—	—
Isopropyl alcohol*	1.8	2.3	2.1	2.2
Methanol*	2.7	—	2.6	2.7

* With the addition of 2,4,6-trimethylphenol (10^{-2} mol L^{-1}) as a hydrogen donor.

Unlike those of ketyl radicals, the k_H values for the similar H atom radical-donors, neutral semiquinone radicals, vary significantly as the structure of the semiquinone radicals changes. Thus, dioxygen does not particularly react at atmospheric pressure with the 1,4-benzosemiquinone and durosemiquinone radicals ($k_H \ll 10^5$ mol L^{-1} s^{-1}), reacts comparatively slightly with the 1,4-naphthosemiquinone radical ($k_H = 6.2 \cdot 10^5$ and $2.3 \cdot 10^5$ mol L^{-1} s^{-1} in a mixture of toluene and 10% isopropyl alcohol and in neat isopropyl alcohol, respectively), but reacts rather efficiently with the anthrasemiquinone radical (Table 2).

The electron-donor ability of neutral $QH^{\cdot}$ radicals may be assumed to vary in parallel with that of the corresponding radical anions $Q^{\cdot -}$. This assumption is confirmed, in particular, by thermodynamic estimates of the energy of the process of electron abstraction from $QH^{\cdot}$, which can be presented as the sequence of the processes of deprotonation of $QH^{\cdot}$, electron abstraction

Table 2. The rate constants of the reaction of the neutral semiquinone radical of anthraquinone with dioxygen in different solvents

Solvent	$E_T(30)$[a]	B[b]	E[c]	$k_H \cdot 10^{-7}$ /mol L^{-1} s^{-1}	Solubility of O_2 /mol L^{-1} (1 atm, 20 °C)	Reference
C_6H_6+3.3% Pr^{i}OH	34.5	48	2.1	22.0	$7.71 \cdot 10^{-3}$	13
MePh	33.9	58	1.3	23.0	$7.59 \cdot 10^{-3}$	
MePh+7.5% Pr^{i}OH				9.2	—	
Dioxane	36.0	237	4.2	11.0	$7.23 \cdot 10^{-3}$	
Dioxane+5% Pr^{i}OH				10.0	—	
$CHCl_3$	39.1	14	3.28	15.0	$8.81 \cdot 10^{-3}$	13
$CHCl_3$+5% Pr^{i}OH				9.5	—	
EtOAc	38.1	181	—	11.0	$8.88 \cdot 10^{-3}$	14
MeCN+5% Pr^{i}OH	46.0	160	5.2	12.0	$8.00 \cdot 10^{-3}$	13
DMF+1.4% Pr^{i}OH	43.8	291	2.6	0.51	$4.76 \cdot 10^{-3}$	13
DMSO+1.8% Pr^{i}OH	45.0	362	3.2	0.082	$2.08 \cdot 10^{-3}$	
Pentanol	49.1	230	~7	0.39	$7.59 \cdot 10^{-3}$	
3-Methyl-1-butanol	46.5	232	7.4	0.38	$7.14 \cdot 10^{-3}$	
Pr^{i}OH	48.6	236	8.7	0.28	$1.03 \cdot 10^{-2}$	14
MeOH	55.5	218	14.9	0.60	$1.03 \cdot 10^{-2}$	14
H_2O+14% Pr^{i}OH	63.1	156	21.8	1.6	$3.41 \cdot 10^{-3}$	

[a] Dimroth—Reichardt's solvation parameter.[17]
[b] Nucleophilicity.[18]
[c] Electrophilicity.[18]

from $Q^{\cdot -}$, and protonation of Q. Then the value of the redox potential $E^0(Q/Q^{\cdot -})$ can serve as the measure of the electron-donor ability of $QH^{\cdot}$: the more negative this potential, the greater the electron-donor ability of $Q^{\cdot -}$, and hence of $QH^{\cdot}$. Since $E^0(Q/Q^{\cdot -})$ = 0.293, 0.050, and −0.266 V for 1,4-benzoquinone, 1,4-naphthoquinone, and anthraquinone, respectively,[9,11] the electron-donor ability of $QH^{\cdot}$ radicals may be assumed to increase in the same series. As the results of the present work showed, k_H for the reaction of $QH^{\cdot}$ with O_2 increases in the same series. This allows one to conclude that this reaction proceeds *via* a transition state in which the charge is transferred from the radical to O_2. The reactions of H atom transfer from ketyl radicals to pyrazolone, indoaniline, and benzoylacetanilide azomethine dyes[15] and to nitroxyl radicals, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl and 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl,[16] proceed similarly. The rate constants of these reactions decrease when the H atom is replaced with D in the semiquinone radical (Table 3).

The deuterium kinetic isotope effect $\beta = k_H/k_D$ for the reaction of the anthraquinone semiquinone radical with O_2 is lower than that for the reaction of ketyl radicals with AD and higher than that for the reaction of ketyl radicals with nitroxyl radicals. The β values are 4.2[19] and below 1.5[16] for the reactions of the ketyl radical of benzoylbenzoic acid with the methylsubstituted pyrazolone azomethine dye and of the ketyl radicals of benzophenone and benzoylbenzoic acid with 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, respectively, whereas β is up to 2.6 (in dioxane) for the reaction of the anthrasemiquinone radical with O_2, which points to moderate weakening of the O—H bond of the semiquinone radical in the transition state of the reaction[20]

$$QH^{\cdot} + O_2 \rightarrow Q + HO_2^{\cdot}. \qquad (11)$$

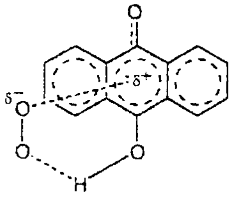
The fact that the isotope effect is lower than the maximum β = 10—13 attainable in this reaction[19,20] can be explained by the nonlinearity of the reaction transition state as well as by the assumption that the H atom in this state is located asymmetrically and is strongly shifted toward the semiquinone O atom[19,20].

Thus, similar to the reaction of ketyl radicals with AD and nitroxyls, the O—H bond of the radical is weakened and a new bond between the H atom and the O_2 molecule forms in the transition state of the reaction of the anthrasemiquinone radical with O_2. Furthermore,

Table 3. The deuterium isotope effects of the reaction of the neutral semiquinone radical of anthraquinone with dioxygen in different solvents

Solvent	k_H, $k_D \cdot 10^{-7}$ /mol L^{-1} s^{-1}	k_H/k_D
Benzene+5% Pr^{i}OH	20.0	
Benzene+5% i-C_3D_7OD	10.0	2.0
Dioxane	11.2	
Dioxane-d_8	4.65	2.4
Dioxane+5.6% Pr^{i}OH	10.5	
Dioxane-d_8+5.6% i-C_3D_7OD	4.0	2.6
$CHCl_3$+5.6% Pr^{i}OH	9.51	
$CDCl_3$+5.6% i-C_3D_7OD	8.11	1.2
MeCN+5.7% Pr^{i}OH	11.3	
MeCN+5.7% i-C_3D_7OD	7.56	1.5

partial transfer of an electron from the radical to O_2 occurs in the transition state; therefore, in this case the electron and proton transfers proceed by a concerted mechanism. Previously,[16,19] it was suggested that for the reaction of ketyl radicals with AD and nitroxyls, the transition states had cyclic structures in which the α-C atom of the ketyl radical served as an electron-donor center and its OH group served as a proton-donor center. A similar cyclic transition state may be also suggested for the reaction of $QH^\cdot$ with O_2. However, it should be taken into consideration that the lone electron is delocalized over the phenyl rings in semiquinone radicals;[21] therefore, these rings can serve as electron-donor centers, and the transition state can be shown as follows:



Thus, the reaction centers of electron and proton transfer are different in the semiquinone radical, which was also observed earlier for ketyl radicals.[16,19] On the basis of the above analysis, we may propose that the proton in the transition state is located closer to the radical, as if it "lags" behind the transferred electron.

Effect of the solvent on k_H for anthrasemiquinone radicals. In the present work, the effect of the solvent on k_H for the semiquinone radical of 9,10-anthraquinone was studied in detail. It is known[12,22,23] that the reactivity of radicals in different solvents is well described by the solvation parameters $E_T(30)$, E, and B (Dimroth—Reichardt's parameter,[17] electrophilicity, and nucleophilicity,[18] respectively).

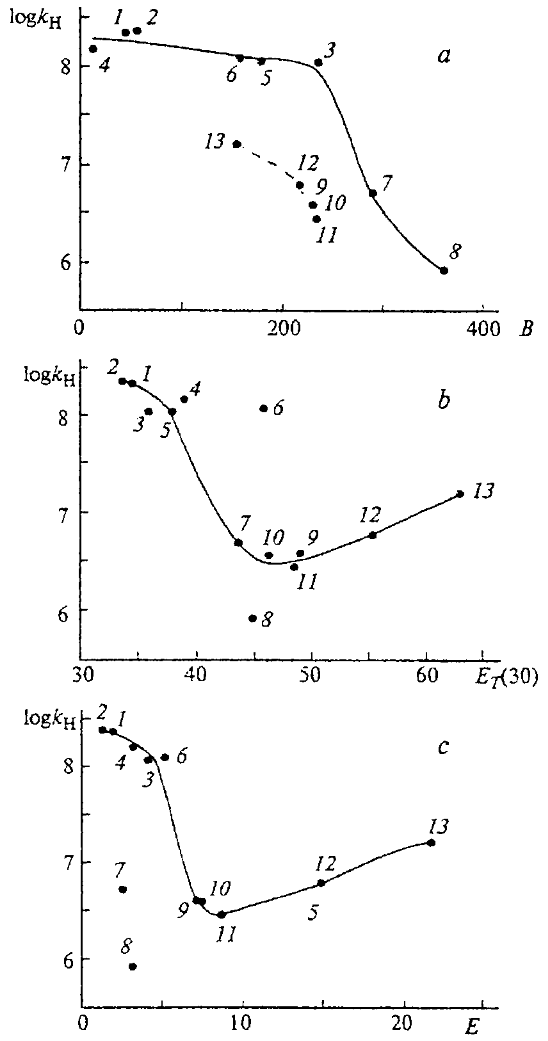


Fig. 1. Dependences of k_H for the reaction of the neutral semiquinone radical of anthraquinone with dioxygen on nucleophilicity B (*a*), Dimroth—Reichardt's solvation parameter $E_T(30)$ (*b*), and electrophilicity E (*c*) of the solvent. *1*, C_6H_6+3.3% Pr^iOH; *2*, MePh; *3*, dioxane; *4*, $CHCl_3$; *5*, EtOAc; *6*, MeCN+5% Pr^iOH; *7*, DMF+1.4% Pr^iOH; *8*, DMSO+1.8% Pr^iOH; *9*, pentanol; *10*, 3-methyl-1-butanol; *11*, Pr^iOH; *12*, MeOH; *13*, H_2O+14% Pr^iOH.

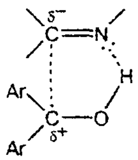
Figure 1, *a* shows the dependence of logk_H for the reaction of the neutral anthrasemiquinone radical with O_2 on the nucleophilicity B of the solvent. It can be seen that the curve falls into two branches, one for aprotic solvents (solid line) and one for protic solvents (dashed line). In aprotic solvents k_H varies only slightly as B increases to $B = 237$. At higher values of B, k_H drops sharply. Strong nucleophilic solvation apparently decreases the reactivity of neutral semiquinone radicals, as was also observed in the case of ketyl radicals;[12] this can be the result of solvation of the H atom of the hydroxyl group of the semiquinone radical such that $^\cdot$O—Ar—OH...:M (M is a molecule of a nucleophilic solvent), which hinders the possible formation of a hydrogen bond between the radical and O_2 and the formation of the corresponding transition state. Weak nucleophilic solvation in aprotic solvents with $B < 237$ does not create much hindrance, apparently due to the high reactivity of O_2 in this reaction. Nonspecific solvation also has no significant effect on k_H. Thus, *e.g.*, in acetonitrile (dielectric constant ε is 36) k_H is close to those in ethyl acetate (ε is 6), chloroform (ε is 4.7), and dioxane (ε is 2.21), and is only two times lower than those in benzene and toluene (ε is 2.3—2.4) (*cf.* Table 2). The logk_H values in Fig. 1, *a* for protic solvents (alcohols and water, dashed line) are well below the corresponding values for aprotic solvents. We can assume that solvation of semiquinone radicals in protic solvents is not completely described by the parameter B, and a decrease in the reactivity in these solvents is more significant than in aprotic solvents with the same B

values. As B increses, a monotonic decrease in k_H is also observed in the series of protic solvents (*cf.* Fig. 1, *a*).

Taking into consideration the controlling influence of nucleophilic solvation on the reactivity of semiquinone radicals, we can also explain the dependences of $\log k_H$ for this reaction on Dimroth—Reichardt's parameter $E_T(30)$ and on the electrophilicity E of the solvent (*cf.* Figs. 1, *b* and 1, *c*). The curves are *V*-shaped, as for the interaction of ketyl radicals with AD and nitroxyls.[12,16] However, at low values of $E_T(30)$ and E ($E_T(30) < 40$ and $E < 6$), the k_H constants vary only slightly as $E_T(30)$ and E vary. The exceptions are the values of $\log k_H$ (points *7* and *8*) in dimethylformamide with 1.4% Pr^{i}OH and in dimethyl sulfoxide with 1.8% Pr^{i}OH (*cf.* Fig. 1, *c*), which is a consequence of the fact that the nucleophilicity of the solvents in these regions of $E_T(30)$ and E is low, and exerts no effect on the reactivity of semiquinone radicals. Of the solvents with $E < 5$ used, only dimethylformamide and dimethyl sulfoxide possess high nucleophilicity ($B = 291$ and 362), which decreases k_H and causes the corresponding points to drop out (*cf.* Fig. 1, *c*). The minima of the dependences of $\log k_H$ on $E_T(30)$ and E correspond to solvents with $E_T(30) = 43-49$ and with $E = 7-9$, and are due to the fact that this region of the curve corresponds to protic solvents (alcohols), which decrease the reactivity of semiquinone radicals. In the series of solvents with $E_T(30)$ values in the range from 43 to 49, only dimethylformamide and dimethyl sulfoxide are aprotic, and the $\log k_H$ values for these solvents "drop out" of the smooth plot (*cf.* Fig. 1, *b*). The $\log k_H$ value in dimethyl sulfoxide lies below the curve due to the high nucleophilicity of dimethyl sulfoxide, and the corresponding value in acetonitrile is above the curve due to the comparatively low nucleophilicity of the solvent ($B = 160$), which exerts practically no effect on the reactivity of semiquinone radicals. The close $\log k_H$ values in dimethylformamide ($B = 291$) and in protic solvents may imply a decrease in the reactivity of semiquinone radicals in dimethylformamide similar to the decrease in alcohols with much lower B (230—236).

As can be seen in Figs. 1, *b* and 1, *c*, a moderate rise in the plots of $\log k_H$ *vs.* $E_T(30)$ and E is also observed in the right-hand region at $E_T(30) > 49$ and $E > 9$. These branches of the plots correspond to protic solvents with high electrophilicity (water, methanol). It is possible that, as for ketyl radicals,[12] the increase in k_H for semiquinone radicals in water (and partly in methanol) is due to the increased electrophilicity of water and hence to $^{\cdot}$O—Ar—(H)O:...H—OH electrophilic solvation of semiquinone radicals, which increases the proton-donor ability of the radical and facilitates the formation of the possible hydrogen bond with O_2. The fact that the nucleophilicity of water and methanol is lower than that of other protic solvents may also contribute to the increase in k_H in these solvents.

Processes of concerted electron—proton transfer. As a generalization of the kinetic data on H atom transfer involving ketyl and neutral semiquinone radicals (the data of the present work and of other works[12,15,16,19]), we may conclude that these reactions are processes of concerted electron and proton transfer. As shown earlier for the reaction of ketyl radicals with AD,[15,19] as well as for the reduction of carbonyl compounds by ketyl radicals,[24] the activation energies of these reactions are rather low (E_a = 13 kJ mol^{-1} for the transfer of an H atom from a benzophenone ketyl radical to AD in isopropanol,[15] $E_a \approx 0$ for the same reaction in toluene and water;[15,19] E_a = 9.6 and 2.1 kJ mol^{-1} for the transfer of an H atom from the dimethylketyl and 4-*tert*-butyldiphenylketyl radicals, respectively, to benzophenone in acetonitrile[24]). Estimates made earlier[24] have shown that, if electron transfer occurs in the first stage of these reactions and then proton transfer occurs (or the reverse), their energy barrier should be very high (in particular, 233 kJ mol^{-1} for the reaction of dimethylketyl with benzophenone in acetonitrile). Based on this, it was concluded that ketyl radicals act as reducing agents with simultaneous abstraction of an electron and a proton, and a considerable fraction of the evolved energy is due to the formation of the double carbonyl bond. In turn, the ketones or AD being reduced in this process serve as simultaneous acceptors of an electron and a proton. As mentioned above, unlike "normal" H atom transfer, in this case the centers of electron and proton transfer are different (the α-C atom and the OH group of ketyl, respectively), which leads to a cyclic structure of the transition state that appears for AD as [19]



Electron and proton transfers that proceed simultaneously but follow different directions "help" each other: the electron transfer provides the appearance of a positive charge on the ketyl radical, which favors deprotonation, whereas proton abstraction from the ketyl radical provides the appearance of a negative charge, which stimulates further electron transfer. This explains the comparatively low energy barrier for these reactions. As shown earlier,[15,16,19] an increase in the electron-donor ability of the ketyl and in the electron acceptor properties of the H atom acceptor increases the reaction rate by increasing the degree of charge transfer from the ketyl to the acceptor in the transition state. On the other hand, the formation of a hydrogen bond between the ketyl and the acceptor also favors the reaction and stimulates electron transfer (and hence proton transfer) from the ketyl to the acceptor. Therefore, not only is strong electron-acceptor ability important for the acceptor in this reaction, but proton-acceptor ability is also important. Hence, for reactions involving reduction by ketyl and neutral semiquinone radicals simultaneous concerted electron and proton transfer is energetically the most favorable pathway of the process. The high rate constants of the reaction of ketyl radicals with O_2 are apparently also due to this mechanism. As can be seen in Figs. 1, *b* and 1, *c*, a *V*-shaped dependence of the reaction rate on the solvation parameter $E_T(30)$ (or electrophilicity E) of the solvent is characteristic of this type of reaction of ketyl radicals. The rate constant is greatest in inert solvents (with minimum $E_T(30)$), which do not hinder the formation of a hydrogen bond between the reactants, and in water (with maximum $E_T(30)$), which increases the proton-donor ability of ketyl radicals due to electrophilic solvation and hence increases the strength of the hydrogen bond. As shown earlier, a similar dependence on the solvent is also characteristic of other reactions of ketyl radicals, in particular, of their recombination to form pinacol.[12] This fact may suggest that recombination of ketyl radicals, despite giving other final products, proceeds *via* an analogous transition state (or weak complex) with a hydrogen bond between two ketyl radicals, and electrophilic solvents increase the reaction rate by facilitating this hydrogen bond.

Similar processes of concerted electron and proton transfer are characteristic not only of reactions of ketyl or semiquinone radicals. *E.g.*, quenching of the triplet state of quinones by phenols proceeds similarly.[25] As mentioned earlier,[25] such reactions should be included in a special class of "ultrafast" processes of H atom transfer, in comparison, *e.g.*, with reactions of H atom abstraction by aliphatic radicals, when the H atom is transferred as a unit. The high efficiency of these processes is due to the combination of strong donor-acceptor interactions involving an electron and a proton.

Analogous cases of mutual stimulation of electron and proton transfer have also been noted in other processes. Thus, *e.g.*, it was shown by picosecond laser photolysis[26] that in the reduction of the benzophenone triplet state by diphenylamine, a charge transfer complex that is extremely short-lived and nonrelaxed relative to solvation, is initially formed in the collision of the reactants; this complex favors the formation of a ketyl radical (*i.e.*, hydrogen transfer) or a relaxed ion pair, depending on the mutual orientation of the reactants in the complex. Hence, in this case the initial charge transfer stimulates further H atom transfer. Quenching of excited singlet 1-pyrenol by pyridine and methylpyridine in nonpolar solvents was studied by femtosecond laser photolysis; it was found that at the beginning of the process electron transfer coupled with the transfer of a considerable fraction of a proton from pyrenol to pyridine occurs.[27] It was also shown in this work that, upon quenching of excited singlet 1-aminopyrene by pyridine and methylpyridine in hexane, a hydrogen bond formed between the reactants that lowered the energy of the ion pair by more than 1 eV at the expense of a small shift of the proton from aminopyrene to pyridine, which considerably facilitated electron transfer in the same direction. Tautomeric transformations of excited singlet 6-hydroxyquinoline in an aqueous medium are also accompanied by concerted transfers of a proton and (intramolecular) an electron, which apparently also occur during the formation of tautomers of other classes of bifunctional molecules.[28] Ultrafast photoinduced concerted electron—proton transfer was observed during photoexcitation of water by femtosecond UV laser pulses.[29] Hence, we may conclude that concerted processes of electron and proton transfers are rather common in reactions involving excited molecules and radicals.

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