HYDROGEN TRANSFER FROM KETYL RADICALS TO NITROXYL RADICALS

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The transfer of an H atom from a ketyl radical (KR) to a nitroxyl radical is the sole reaction occurring between benzophenone or acetone KR and nitroxyl radicals (NR). The rate constants (k_H) of the reaction of the KR of substituted benzophenones with the NR - 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl and 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl in various solvents were measured by the pulse photolysis method. In low-viscosity solvents (up to 1-2 cP), the values of k_H are not limited by the diffusion of the reagents. The k_H values decrease with increase in the Hammet's σ -constants of the substituents in the KR and with decrease in the reduction potential of the NR, which indicates a charge transfer from the KR to NR in the transition state. The reaction. A cyclic structure was proposed for the transition state. The reaction is characterized by a low isotopic effect (k_H/k_D = 1.4-1.5). The dependence of log k_H on the solvation parameter of the solvent E_t(30) is V-shaped in character.

The use of photoreduction reactions in which ketyl radicals participate has gained a wide acceptance in photochemistry. Ketyl radicals (KR) effectively reduce nitro compounds, quinones [1], azomethine dyes (AD) [2, 3], and other dyes [4, 5] and ketones [6]. An H atom transfer possibly also occurs in the reactions of several KR with nitroxyl radicals (NR) [7, 8]. It was shown in the present work that hydrogen transfer is the sole reaction of benzophenone and acetone KR with NR, and the rate constants of the hydrogen ($k_{\rm H}$) and deuterium ($k_{\rm D}$) atom transfer from the KR of substituted benzophenones to NR were measured in various solvents using pulse photolysis.

EXPERIMENTAL

The KR were obtained by photoexcitation of deoxygenated solutions (~ 10^{-3} M) of benzophenone (BP), 4,4'-dimethylbenzophenone (DMBP) and 4-benzoylbenzoic acid (BBA) in isopropanol, MeOH, ethylene glycol, pyridine, CHCl₃, toluene, mineral oil, and water (with the addition of 4% of ethanol). The carbonyl compounds in a triplet state thus split off the hydrogen atom from the solvent and form the corresponding KR. The deuterated KR were obtained by a triplet state of the carbonyl compounds splitting off a D atom from a deuterated solvent - methanol-d₄. Nitroxyl radicals having the following structure were used



Reaction products of KR with NR accumulated during the photolysis of deoxygenated solutions containing (I) ($\sim 3 \cdot 10^{-2}$ M) and benzophenone ($\sim 5 \cdot 10^{-1}$ M) or acetone (~ 5 M) in isopropanol using a DRSh-500 mercury lamp with UFS-6 (benzophenone) or UFS-5 light filters (acetone). Thus, most of the light absorbed by the solution was absorbed by the benzophenone or acetone.

The k_H (k_D) values were measured according to the acceleration of the decay kinetics of the KR, recorded on a pulse photolysis apparatus ($\tau_{1/2} = 5 \mu sec$, energy 50 J) by introducing the NR into the system (5·10⁻⁶-5·10⁻⁴ M, recording wavelength 540-560 nm, determination error of k_H (k_D) ±10%). The solvents used were chemically pure grade isopropanol and toluene,

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KR (σ*)		Solvent characteristic			k _H ·10 ⁻⁷ , M ⁻¹ ·sec ⁻¹	
	Solvent	η, cP (20°C)	E _t (30)	в†	NR (1) (-0.40 V)‡	NR (II) (-0.34 V)‡
DMBP (-0,34)	Isopropano1	1,77	48,6	236	_	7,1
BP (0)	Pyridine Isopropanol Methanol Ethylene glycol Water Chloroform Toluene	0,974 1,77 0,597 19,9 1,005 0,580 0,590	40,2 48,6 55,5 56,3 63,1 39,1 33,9	472 236 218 224 156 14 58	1,3 3,4 4,4 1,3 8,0 22 87	5.7 6,7 12 100
BBA (0,42)	Isopropanol Methanol	1,77 0,597	48.6 55,5	236 218	2,3	2,3

TABLE 1. Rate Constants (k_H) of the Reaction of KR of Substituted Benzophenones with NR (I) and (II) in Various Solvents

*The Hammet's constants of substituents of benzophenone KR. *Nucleophilicity of solvents according to [9]. *Polarographic reduction potentials of NR in ethanol [10].

"analytically pure" grade ethylene glycol, and medicinal grade mineral oil, and also chloroform, pyridine, methanol- h_4 and methanol- d_4 and water, which were purified by distillation. The substituted benzophenones were purified by recrystallization and sublimation. A specially pure grade acetone was used. The solutions were deoxygenated by purging with Ar and by the freezing and thawing method. The absorption spectra were recorded on a "Specord UV-VIS" spectrophotometer. The viscosity of the toluene-mineral oil and methanol-ethylene glycol mixtures was measured on a Heppler viscosimeter. The experiments were carried out at 20 \pm 1°C.

RESULTS AND DISCUSSION

During the photolysis of the deoxygenated solutions of (I) in isopropanol in the presence of excess benzophenone or acetone, the solution becomes decolorized due to the consumption of the NR, which is seen from the absorption spectra (the band with $\lambda_{max} = 460$ nm decreases). On saturation of the photolyzed solutions with oxygen, complete regeneration of the initial NR is obtained in the course of 2-3 days. It is clear that as a result of the photochemical reaction a single product is formed from the NR, namely, 1,4-dihydroxy-2,2,6,6tetramethylpiperidine, which in the presence of oxygen slowly oxidizes to the initial NR, while no recombination products of KR with NR are formed. Thus, the process of the H atom transfer from KR to NR with the formation of the corresponding hydroxylamine is the only route for the consumption of NR in this system



The rate constants of the hydrogen transfer k_H are given in Table 1.

We shall now consider the dependence of $k_{\rm H}$ on the viscosity of the solvent. In the reaction of the KR of benzophenone with NR in various solvents, their viscosity η (except for ethylene glycol and isopropanol) changes by not more than twofold; at the same time, their $k_{\rm H}$ (for NR (I)) changes by a factor of more than 70 (see Table 1). Hence, in this case, the change in the viscosity of the solvent is not the main reason for the change in $k_{\rm H}$. We have also measured the $k_{\rm H}$ values for the reaction of benzophenone KR with NR (I) in binary mixtures of solvents of different viscosities: toluene-mineral oil and MeOH-ethylene glycol (the two mixture components were selected with a similar solvating power). In a mixture containing 25% of mineral oil (η = 0.96 cP), the value of $k_{\rm H}$ = 8.4 $\cdot 10^8$ M⁻¹ $\cdot \rm sec^{-1}$ is close to that of $k_{\rm H}$ in pure toluene (see Table 1), and only in a mixtures of MeOH with 20% of ethylene glycol



Fig. 1. Dependence of $\log k_H$ for the reaction of benzophenone KR with NR (I) (1') and (II) (2') on the solvation parameter of the solvent $E_t(30)$: 1) hexane; 2) chloroform; 3) pyridine; 4) isopropanol; 5) methanol; 6) water.

Fig. 2. Dependence of $\log k_H$ for the reaction of benzophenone KR with NR (I) (1') and (II) (2') on the nucleophilicity of the solvent B (the numerals at the points correspond to the numbers of the solvents in Fig. 1).

 $(\eta = 1.07 \text{ cP})$ and 40% of ethylene glycol $(\eta = 1.93 \text{ cP}) k_{\text{H}} = 4.3 \cdot 10^7 \text{ and } 4.0 \cdot 10^7 \text{ M}^{-1} \cdot \text{sec}^{-1}$, respectively, which is close to the k_{H} in pure MeOH, and only in ethylene glycol $(\eta = 19.9 \text{ cP})$, k_{H} decreases by a factor of 3.4 (see Table 1). Thus, in low-viscosity solvents with $\eta \leq 2 \text{ cP}$ (in weakly solvating solvents — with $\eta < 1 \text{ cP}$), the value of k_{H} (k_{D}) is not limited by the diffusion of the reagents, and is located in a kinetic region.

The dependence is observed of the $k_{\rm H}$ value on the redox properties of the KR-NR system. The value of $k_{\rm H}$ in one and the same solvent decreases with increase in the Hammet's σ -constants of the substituents in the KR and with decrease in the reduction potential of the NR. This indicates that a charge transfer occurs from KR to NR in the transition state of the hydrogen transfer reaction, similarly to the reaction of KR with an AD [11]. The value of $k_{\rm H}$ increases on transition from pyridine and alcohols to weakly-solvating solvents – toluene and chloroform, which indicates the presence of an H-bond between the KR and NR in a transition state. Since the O' atom of the nitroxyl is probably an H-bond acceptor, and the N-atom is an electron-acceptor, while the α -C-atom of the transition state of this reaction can be depicted as follows



Unlike the reaction of AD, the kinetic isotopic effect is relatively weak in this reaction. In particular, in methanol for NR (I) and the BP and BBA ketyls, $k_D = 3.0 \cdot 10^7$ and $1.6 \cdot 10^7 \text{ M}^{-1} \cdot \text{sec}^{-1}$, respectively, whereby $k_H/k_D = 1.4 \cdot 1.5$ (for the reaction of KR with AD, the k_H/k_D value reaches 4.2 [11]). The character of the substituents in the KR practically does not influence the k_H/k_D value. This indicates a sharp asymmetry of the disposition of the H atom between the ketyl O atom and the O' of the nitroxyl in the transition state (the O-H bond of the ketyl is only slightly weakened), caused probably by steric hindrances to the approach of the KR to NR (with four CH₃ groups in the NR).

The influence of the nature of the solvent on the reaction rate is illustrated in Figs. 1 and 2, where the dependences of $\log k_H$ on the solvation parameter $E_t(30)$ and the nucleophilicity of the solvent B [12] are depicted. The dependence of $\log k_H$ on $E_t(30)$ (Fig. 1) is V-shaped in character with a minimum corresponding to a strong nucleophile-pyridine and

ascends in the regions of nonsolvating solvents and water, similarly to the reaction of KR with AD [13]. The reason for this is that the nucleophilic solvents lower the reactivity of the KR, while the electrophilic solvents (particularly water) increase it. However, in the presence of electrophilic solvents (water, MeOH), the ascent in this region is much less sharp than in the case of AD [13], probably due to the fact that the electrophilic solvents lower the reactivity of the NR due to the solvation of the 0 atom of the N-O' group [14]. This somewhat compensates for the increase in the reactivity of KR in electrophilic solvents. This also explains the relatively low values of $k_{\rm H}$ in the electrophilic solvent - chloroform with practically no nucleophilicity: the point corresponding to chloroform practically does not deviate from the V-shaped curve in Fig. 1 (reflecting the influence of the electrophilicity of the solvent), although for the reaction of the KR with AD the points corresponding to chloroform and certain other chlorine-containing solvents lie much higher than for the nucleophilic solvents with similar values of $E_t(30)$ and sharply deviate from the V-shaped dependence [13]. The dependence of $\log k_H$ on B (Fig. 2) has the same character as for AD [13] (its slope decreases with increase in B), but the point for water does not deviate from it, and for chloroform it is located much lower than for toluene, having a similar value of B. This is probably also due to a decrease in the reactivity of the NR in electrophilic solvents - water and chloroform. Thus, the increase in the nucleophilicity of the solvent leads to a decrease in the $k_{\rm H}$ due to the nucleophilic solvation of the KR and decrease in its reactivity [13]. At the same time, increase in the electrophilicity of the solvent does not act unequivocally on k_{H} : it results in a decrease in the reactivity of the NR (in strongly electrophilic solvents of the water and methanol type) and in increase in the reactivity of the KR.

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