Flash Photolysis Studies of Phenyl-substituted Phenols, Quinones, and Corresponding Free Radicals. Part 4.† Kinetics and Mechanism of the Elementary Reaction of Oxidation of Aliphatic Alcohols by Aroxyl Radicals

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The kinetics of the elementary reaction between the 2,6-diphenyl-4-stearoxyphenoxyl radical (PsO$^•$) with C_1—C_4 aliphatic alcohols in the corresponding alcohols or benzene–alcohol mixtures has been investigated. It has been found that k is *ca.* 10^{-3}—10^{-6} l mol^{-1} s^{-1} at 338 K. The reactions have characteristically high activation energies E_a = 40—75 kJ mol^{-1} and low pre-exponential factors A = 10^1—10^7 l mol^{-1} s^{-1}. An increase of the alcohol content in benzene inhibits the reaction due to formation of the less reactive PsO$^•\cdots$alcohol complexes. Using an *N*-benzylidene-t-butylamine oxide spin trap, alcohol radicals have been detected and the elementary reaction mechanism has been established: at 373 K primary alcohols and t-butyl alcohol are oxidized primarily by way of electron transfer, and secondary alcohols predominantly by hydrogen atom abstraction (the solvent is the corresponding alcohol). At 338 K the reaction is selective: in pure alcohols and benzene containing 5% alcohol the reaction route which had been dominant becomes the only possible one.

Aroxyl radicals oxidize compounds containing a nucleophilic heteroatom or a labile hydrogen atom.[1–6] The aroxyl radicals are usually thereby converted into the corresponding phenols or cyclohexadienones.[1–6] Reactions involving hydrogen atom abstraction by aroxyl radicals have a strong, and sometimes even decisive, effect on the inhibition of oxidation of organic compounds by hydroxyaromatic compounds.

The mechanism of oxidation (or dehydrogenation) of organic compounds containing a mobile hydrogen atom by radicals appears, at present, under discussion (*cf.*, *e.g.* refs. 1—3 and 7—9). The elementary reaction may be either hydrogen atom abstraction or electron transfer. The hydrogen abstraction *versus* electron transfer alternative is of a quite general nature. To establish the true mechanism it is absolutely necessary to trap the elementary reaction products immediately.

This work is devoted to an investigation of the kinetics and mechanism of oxidation of aliphatic alcohols by aroxyl radicals, *viz.* 2,6-diphenyl-4-stearoxyphenoxyl (PsO$^•$) and sometimes also galvinoxyl (G$^•$). 2,6-Diphenyl-4-stearoxyphenol is one of the most effective polyolefin degradation inhibitors[5] and investigation of PsO$^•$ reactivity is of practical interest.

Experimental

The reactants used were 2,6-diphenyl-4-stearoxyphenol (PsOH), twice recrystallized from ethanol, distearyl thiodipropionate (DSTDP) also twice recrystallized from ethanol, chromatographically pure benzene, and the aliphatic alcohols CH_3OH, CH_3OD, and CD_3OD, EtOH, Pr^{n}OH, Pr^{i}OH, Bu^{n}OH, Bu^{s}OH, and Bu^{t}OH. *N*-Benzylidene-t-butylamine oxide (PBN) was used without further purification. Galvinoxyl (G$^•$) was prepared according to ref. 10. The PsO$^•$ solutions were obtained by oxidation of PsOH solutions with lead dioxide. The initial concentrations of radicals were $[PhO^•]_0$ *ca.* 5×10^{-5}M and $[G^•]_0$ *ca.* 8×10^{-5}M. PBN was added to the solutions in amounts ranging from 5×10^{-2} to 5×10^{-1}M. The absorption spectra of solutions were recorded using the Specord u.v.–visible spectrophotometer in l = 1 cm cells. In the kinetic experiments the absorption spectra were taken at equal periods of time Δt = 5(10) min or the spectrophotometer was switched to the kinetics recording mode. The aroxyl radical decay kinetics were monitored according to the variation of optical density at absorption maxima λ 405 [ε $(2.5 \pm 0.5) \times 10^4$ l mol^{-1} cm^{-1}] or 650 nm [$(2.5 \pm 0.2) \times 10^3$] (for radical PsO$^•$[11]) and at λ 432 nm (ε 1.54×10^5 l mol^{-1} cm^{-1}) (for radical G$^•$[12]). The e.s.r. spectra of deoxygenated solutions were recorded with the Varian E-12A spectrometer; the error of determination of h.f.s. constants was ±0.05—0.10 Oe. All solutions were thermostatted and, when necessary, deoxygenated by the passage of argon. Kinetic experiments were carried out in the temperature ranges 273—299 and 338—345 K. Activation energies E_a and pre-expontential factors A were determined from Arrhenius plots for which the temperature range was not less than *ca.* 50 °C.

Results

Kinetics.—No aroxyl consumption was observed after thermostatting the PsO$^•$ and G$^•$ solutions in benzene at 338 K for 6 h and at 373 K for 30 min. When alcohols (R^1R^2CHOH)‡ were added to the test solutions aroxyl radicals began to be consumed. Reaction (1) takes place in a solution of the aroxyl in

$$PsO^• + R^1R^2CHOH \longrightarrow PhOH + \text{alcohol radical} \quad (1)$$

R^1R^2CHOH or a benzene–R^1R^2CHOH mixture. Radical G$^•$ participates in a similar reaction. The active alcohol radical is, apparently, immediately trapped by G$^•$ present in an excess relative to the alcohol radicals[4] [reaction (2)]. In the case of

$$G^• + \text{alcohol radical} \longrightarrow \text{non-radical products} \quad (2)$$

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† Part 3, P. P. Levin, I. V. Khudyakov, V. A. Kuzmin, H. J. Hageman, and C. R. H. I. de Jonge, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1238.

‡ The R^1R^2CHOH denotes all the alcohols investigated, Bu^{t}OH included.

Table 1. Rate constants at 338 K, activation energies, pre-exponential factors of reaction (1), bond energies in alcohols, and alcohol ionization potentials in the gas phase

Solvent[a]	k_1[e]/l mol^{-1} s^{-1}	E[f]/ kJ mol^{-1}	A/l mol^{-1} s^{-1}	D(C–H)/ kJ mol^{-1}	D(O–H)/ kJ mol^{-1}	I.P./eV
CH_3OH (3.7M)	1.5×10^{-5}	45				
CH_3OH (100%)	7.5×10^{-6}		62	395	338	10.84
CH_3OD (3.4M)	1.5×10^{-5}					
CD_3OD (3.3M)	5.8×10^{-6}					
EtOH (100%)	3.2×10^{-5}	53	7×10^3	382	428	10.47
Pr^nOH (0.67M)	1.8×10^{-4}					
Pr^nOH (1.33M)	1.5×10^{-4}					
Pr^nOH (1.33M)[b]	8.0×10^{-4}					
Pr^nOH (2.0M)	1.25×10^{-4}					
Pr^nOH (6.65M)	7.5×10^{-5}				429	10.23
Pr^nOH (100%)	7.1×10^{-5}	53	1.0×10^4			
Pr^nOH (100%)[c]	8.8×10^{-6}	45	30			
Pr^nOH (100%)[b,c]	6.4×10^{-5}					
Pr^iOH (6.67M)	6.5×10^{-4}	50	3.3×10^3	370	439	10.12
Pr^iOH (100%)	7.2×10^{-5}					
Bu^nOH (1.64M)	2.1×10^{-4}					
Bu^nOH (100%)	3.1×10^{-5}	67	8.1×10^5	391	424	10.04
Bu^nOH (1.64M)[b]	1.5×10^{-3}					
Bu^sOH (0.55M)	1.2×10^{-3}					
Bu^sOH (1.01M)	7.9×10^{-4}					
Bu^sOH (1.64M)	7.4×10^{-4}	71	6.6×10^7	382		
Bu^tOH (100%)	1.0×10^{-5}	79	1.4×10^7	407	436	9.7
C_6H_6[d]	6.0×10^{-3}					

[a] C_6H_6 containing the following alcohols with the concentrations in parentheses. [b] Solution containing PBN (0.1M). [c] Reaction with G$^•$. [d] Reaction (5). [e] Error *ca.* 10%. [f] Error 2—3 kJ mol^{-1}.

PsO$^•$ reaction of type (2) does not take place and PsOH is the basic reaction product. Indeed, reoxidation of the PsOH product yields PsO$^•$ in a concentration equal to the initial concentration $[PsO^•]_0$ of the radical which took part in reaction (1).

The decay of G$^•$ in Pr^{n}OH solutions followed the pseudo-first-order kinetics and was characterized by a rate constant k_{eff}/s^{-1}. We assume that for reaction (1) with G$^•$, $k_1 = k_{eff}/(2[Pr^nOH])$, where $[Pr^nOH]$ is the concentration of pure Pr^{n}OH (13.3M); the factor 2 in this expression is due to reaction (2) (*cf.*, *e.g.* ref. 4).

Apart from reaction (1), radical PsO$^•$ takes part in the reversible dimerization (3).[11] K_3/mol l^{-1} = k_{-3}/k_3. The K_3

$$2\,PsO^• \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{dimer} \qquad (3)$$

values in C_6H_6, R^1R^2CHOH, and their binary mixtures have been obtained by the flash photolysis technique according to the procedure described in ref. 11. Thus in C_6H_6 at 338 K, $K_3 = (2.2 \pm 0.2) \times 10^{-5}$ mol l^{-1}. For equilibrium (3) in the investigated solutions $\Delta H_3^0 = -60 \pm 2$ kJ mol^{-1}.

The PsO$^•$ decay rate obeys, with the natural assumption that $k_3[PsO^•] \gg k_1[R^1R^2CHOH]$, the rate law (4)[13] where k'_{eff} is

$$-\,d[PsO^•]/dt = k'_{eff}[PsO^•]/(1 + 2[PsO^•]/K_3) \qquad (4)$$

the pseudo-first-order rate constant of the interaction between PsO$^•$ and R^1R^2CHOH [reaction (1)]. The value of k'_{eff} was determined from the slope of the straight line of a plot of $(\ln[PsO^•] + 2[PsO^•]/K_3)$ *versus* t. In a number of cases where $[PsO^•]$ was sufficiently small $(2[PsO^•]/K_3 \ll 1)$ PsO$^•$ decay followed first-order kinetics with the rate constant equal to k'_{eff}. For a high enough $[PsO^•]$ $(2[PsO^•]/K_3 \gg 1)$ PsO$^•$ decay occurred with zero-order kinetics with k/mol l^{-1} s^{-1} = $k'_{eff}K_3/2$. Under the experimental conditions, $k_{eff} \sim [R^1R^2CHOH]$ for $10^{-2} \leqslant [R^1R^2CHOH] \leqslant 0.5$M. The k_1 values were determined from the slopes of the straight lines of a plot of k_{eff} *versus* $[R^1R^2CHOH]$ (Table 1). A further increase of $[R^1R^2CHOH]$ (to more than 5% by volume) produced deviations from the proportionality due to solvent effects. In all cases it was assumed the $k_1 = k'_{eff}/[R^1R^2CHOH]$. The k_1 values thus obtained are listed together with E_a and A in Table 1.

The reaction between PsO$^•$ and DSTDP in C_6H_6 has also been studied. The kinetics of this reaction has been investigated in the same way as that of reaction (1) (see above). Direct proportionality has been observed between the effective rate constant of reaction (5), k''_{eff}, and [DSTDP] in the range

$$PsO^• + \text{DSTDP} \xrightarrow{k_5} \text{PsOH} + \text{DSTDP radical} \qquad (5)$$

$10^{-2} \leqslant [DSTDP] \leqslant 10^{-1}$M. The k_5 values are listed in Table 1. The radicals produced from DSTDP do not react with PsO$^•$: the yield of PsOH in reaction (5) is close to 100% which is in good agreement with the results obtained in parallel investigations.[5] Oxygen did not affect the PsO$^•$ consumption rate and PsOH yield. In air-saturated solutions alcohol radicals transform into peroxide radicals which also, obviously, react with G$^•$ but do not react with PsO$^•$. It is known that PsO$^•$ and G$^•$ do not react with oxygen.[5,10,11]

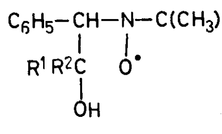
Addition to the solutions containing Pr^{n}OH, Pr^{i}OH, Bu^{n}OH, Bu^{s}OH, and DSTDP of a PBN spin trap accelerated PhO$^•$ and G$^•$ decay in normal alcohols several times but did not affect the PsO$^•$ decay rate in secondary alcohols and rate of reaction with DSTDP. The kinetics of PsO$^•$ and G$^•$ decay in normal alcohols in the presence on PBN fitted well into relationship (4) (the PsO$^•$ radical) and the pseudo-first-order law (the G$^•$ radical). It was assumed that $k_1 = k_{eff}/[Pr^nOH]$ and $k_1 = k'_{eff}/[R^1R^2CHOH]$ for reactions involving G$^•$ and PsO$^•$, respectively.

Spin Trapping.—In order to establish the nature of the radicals produced from the oxidized compounds, reactions (1) and (5) were carried out in the presence of PBN at 338 and 373 K. Thermostatting of the test solutions over the oxidation

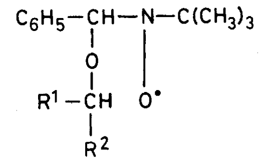
Table 2. Parameters of e.s.r. spectra of spin-adducts

Alcohol	Spin-adduct	Relative[a] amount of $(\mathrm{A_i}^{\bullet})$	H.f.s. constants (Oe)[b]		Relative[a] amount of $(\mathrm{A_i}^{\bullet})$	H.f.s. constants (Oe)[c]	
			a_N	a_{β}^{H}		a_N	$a^{\beta H}$
CH_3OH	$(\mathrm{A_1}^{\bullet})$	§			*		
	$(\mathrm{A_2}^{\bullet})$	*	14.1	2.8	†	14.0	2.8
	$(\mathrm{A_3}^{\bullet})$	‡	14.3		†	14.2	
CH_3OD	$(\mathrm{A_1}^{\bullet})$	§					
	$(\mathrm{A_2}^{\bullet})$	†	13.9	2.6			
	$(\mathrm{A_3}^{\bullet})$	†	14.0				
CD_3OD	$(\mathrm{A_1}^{\bullet})$	§					
	$(\mathrm{A_2}^{\bullet})$	†	13.9	2.6			
	$(\mathrm{A_3}^{\bullet})$	†	14.0				
EtOH	$(\mathrm{A_1}^{\bullet})$	‡	15.0	2.9			
	$(\mathrm{A_2}^{\bullet})$	*	14.3	2.8			
	$(\mathrm{A_3}^{\bullet})$	‡	14.3				
Pr^nOH	$(\mathrm{A_1}^{\bullet})$	§			§		
	$(\mathrm{A_2}^{\bullet})$	*	14.2	2.6	*	14.2	2.3
	$(\mathrm{A_3}^{\bullet})$	‡	13.9		§		
Pr^iOH	$(\mathrm{A_1}^{\bullet})$	*	15.0	3.55	§		
	$(\mathrm{A_2}^{\bullet})$	‡	14.2	2.1	†	13.9	2.1
	$(\mathrm{A_3}^{\bullet})$	§			§		
Bu^nOH	$(\mathrm{A_1}^{\bullet})$	‡	15.0	3.9	§		3.0
	$(\mathrm{A_2}^{\bullet})$	†	14.1	2.7	*	14.5	
	$(\mathrm{A_3}^{\bullet})$	*	14.3		†	15.8	
Bu^sOH	$(\mathrm{A_1}^{\bullet})$	*	15.0	3.4	*	14.9	3.1
	$(\mathrm{A_2}^{\bullet})$	‡	14.3	2.5	§		
	$(\mathrm{A_3}^{\bullet})$	§			§		
Bu^tOH	$(\mathrm{A_1}^{\bullet})$	§					
	$(\mathrm{A_2}^{\bullet})$	†	14.5	2.1			
	$(\mathrm{A_3}^{\bullet})$	§					

[a] * Formation mainly of $(\mathrm{A_i}^{\bullet})$ (*ca.* 10^{-5}M), † formation of $(\mathrm{A_i}^{\bullet})$ (*ca.* 10^{-6}M), ‡ traces of $(\mathrm{A_i}^{\bullet})$ (*ca.* 10^{-7}M), § absence of $(\mathrm{A_i}^{\bullet})$. [b] Reaction was conducted in the corresponding alcohol at 373 K. [c] Reaction was conducted in the corresponding alcohol at 338 K.



$(\mathrm{A_1}^{\bullet})$



$(\mathrm{A_2}^{\bullet})$

reaction period (*ca.* 20 min at 373 K and *ca.* 6 h at 338 K) was not accompanied by consumption of PBN or the appearance of any e.s.r. signals. During the thermostatting of aroxyl solutions in C_6H_6 in the presence of PBN for the same period of time no aroxyl consumption or appearance of any new e.s.r. signals were recorded (blank runs). As reaction (1) went on, the e.s.r. spectrum of $PsO^{\bullet}$ $(G^{\bullet})$ gradually vanished and the e.s.r. spectra of nitroxyl radical(s) of spin-adducts appeared. After reaction (1) was completed the e.s.r. spectra of three different spin adducts were recorded. These were those of hydroxyalkyl radical $(\mathrm{A_1}^{\bullet})$, alkoxyl radical $(\mathrm{A_2}^{\bullet})$, and adduct $\mathrm{A_3}^{\bullet}$ characterized by splitting only at nitrogen (Table 1). On the basis of the ratios of intensities of the e.s.r. signals corresponding to $\mathrm{A_1}^{\bullet}$ one may at least qualitatively compare the concentrations of the resultant spin-adducts (Table 2).

It was not possible to record the spin-adducts of the radicals produced in reaction (5) at 338 K.

Discussion

Oxidation of alcohols by $PsO^{\bullet}$ (or $G^{\bullet}$) may take place either by way of hydrogen atom transfer (1A), whereby α-hydroxyalkyl

$$PsO^{\bullet} + R^1R^2CHOH \longrightarrow PsOH + R^1R^2\dot{C}OH \quad (1A)$$

$$PsO^{\bullet} + R^1R^2CHOH \longrightarrow PsO^{-} + (R^1R^2CHOH)^{+\bullet} \longrightarrow PsOH + R^1R^2CHO^{\bullet} \quad (1B)$$

radicals are formed[*] or by way of electron transfer (1B), whereby alkoxyl radicals are formed. The energy of dissociation of the O–H bond in alcohols (see Table 2) is usually notably greater than that of the α-C–H bonds, therefore, the probability of hydrogen-atom abstraction from the hydroxy group by a radical or carbonyl compound in the triplet state is small (*cf.*, *e.g.*, refs. 14 and 15).[†] It has to be noted that the probability of oppositely charged radical-ions leaving the cage [reaction (1B)] must be small. If a certain number of radical-cations formed in reaction (1B) do leave the cage, they are converted into neutral alkoxyl radicals *via* reaction (6) with R^1R^2CHOH.[16,17] The well known gas-phase reaction (7) is obviously less likely in the liquid phase.[17,18]

$$(R^1R^2CHOH)^{+\bullet} + R^1R^2CHOH \longrightarrow R^1R^2CHO^{\bullet} + R^1R^2CHOH_2^{+} \quad (6)$$

$$(R^1R^2CHOH)^{+\bullet} + R^1R^2CHOH \longrightarrow R^1R^2\dot{C}OH + R^1R^2CHOH_2^{+} \quad (7)$$

Radicals $R^1R^2\dot{C}OH$ and $R^1R^2CHO^{\bullet}$ formed in reactions (1A) and (2B) are accepted by PBN, yielding $(\mathrm{A_1}^{\bullet})$ and $(\mathrm{A_2}^{\bullet})$. Reactions (8) and (9) have high rate constants. Thus k_8 is *ca.*

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[*] Or β-hydroxyalkyl radicals in the case of Bu^tOH.

[†] This is also true for CH_3OH [14,15] for which according to ref. 15, as for other alcohols, *D*(O–H) is *ca.* 428 kJ mol^{-1}.

$$\mathrm{R^1R^2\dot{C}OH + PBN \longrightarrow (A_1{}^{\bullet})} \qquad (8)$$

$$\mathrm{R^1R^2CHO^{\bullet} + PBN \longrightarrow (A_2{}^{\bullet})} \qquad (9)$$

10^9 l mol^{-1} s^{-1} for $\mathrm{CH_3\dot{C}HOH}$ and *ca.* 10^7 l mol^{-1} s^{-1} for $\mathrm{(CH_3)_2\dot{C}OH}$ in the corresponding alcohols (*ca.* 293 K);[16,18] k_9 is *ca.* 10^8 l mol^{-1} s^{-1} for MeO$^{\bullet}$ and EtO$^{\bullet}$ in the corresponding alcohols (*ca.* 293 K)[19] and *ca.* 5.5 × 10^6 l mol^{-1} s^{-1} for Bu^{t}O$^{\bullet}$ (benzene; *ca.* 298 K).[20] Estimates give k_8 *ca.* 10^5 l mol^{-1} s^{-1} for $\mathrm{\dot{C}H_2OH}$ and $\mathrm{\dot{C}H_2C(CH_3)_2OH}$ (*ca.* 313 K).[21] At 338 and 373 K these constants are, naturally, much higher.

There are known conversions (10) of $\mathrm{R^1R^2CHO^{\bullet}}$ into the

$$\mathrm{R^1R^2CHO^{\bullet} \longrightarrow R^1R^2\dot{C}OH} \qquad (10)$$

thermodynamically more stable radicals $\mathrm{R^1R^2\dot{C}OH}$.[22] It is more conventional to assume that at not too high temperatures the isomerization occurs *via* route (11).[19] For $\mathrm{CH_3O^{\bullet}}$, k_{11} is *ca.*

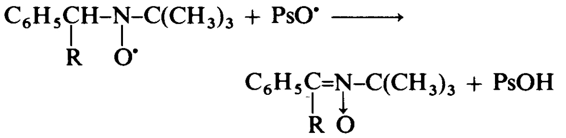
$$\mathrm{R^1R^2CHO^{\bullet} + R^1R^2CHOH \longrightarrow R^1R^2CHOH + R^1R^2\dot{C}OH} \qquad (11)$$

2.6 × 10^5 l mol^{-1} s^{-1} and for $\mathrm{C_2H_5O^{\bullet}}$ *ca.* 1.1 × 10^6 l mol^{-1} s^{-1} (*ca.* 293 K) in the corresponding alcohols.[19] Values in the range 10^5—10^6 l mol^{-1} s^{-1} may be expected[18] for other $\mathrm{R^1R^2CHO^{\bullet}}$ radicals. The radicals $\mathrm{R^1R^2\dot{C}OH}$ may recombine or undergo disproportionation [reaction (12)]. The concentrations of $(\mathrm{A_1{}^{\bullet}})$ and $(\mathrm{A_2{}^{\bullet}})$ remain practically constant at [PBN] ⩾ 0.1M which means that all radicals are accepted. (The case of Bu^{t}OH is an exception and will be discussed below.) Therefore, under the experimental conditions, reactions (8) and (9) almost totally prevail over reactions (6) and (10) (if possible at all in the system in question) as well as (11) and (12). Total acceptance of the radicals produced from alcohols can normally be achieved using PBN or other spin traps in high concentrations (10^{-2}—10^{-1}M).[8,17,19]

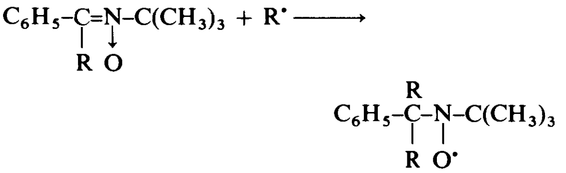
$$\mathrm{2R^1R^2\dot{C}OH} \begin{array}{l} \nearrow \mathrm{R^1R^2C(OH)C(OH)R^2R^1} \\ \searrow \mathrm{R^1C(O)R^2 + R^1R^2CHOH} \end{array} \qquad (12)$$

The parameters of the e.s.r. spectra of $(\mathrm{A_1{}^{\bullet}})$ and $(\mathrm{A_2{}^{\bullet}})$ (Table 2) are consistent with the corresponding published data.[8,17–20,23] The numerical values of a_{N} ($a_{\mathrm{H}}{}^{\beta}$) for the spin-adducts of one and the same radical and in one and the same solvent are sometimes somewhat different (by a few tenths of Oe) as reported by different authors (*cf.*, *e.g.* refs. 18 and 22). However, we believe that it is not difficult to distinguish between radicals $(\mathrm{A_1{}^{\bullet}})$ and $(\mathrm{A_2{}^{\bullet}})$. The general tendency is such that for radical $(\mathrm{A_1{}^{\bullet}})$ in alcohols $a_{\mathrm{N}} \geqslant 15.0$ and $a_{\mathrm{H}}{}^{\beta} \geqslant 3.0$ Oe, and for $(\mathrm{A_2{}^{\bullet}})$ the respective values are smaller, $a_{\mathrm{N}} \leqslant 14.5$ and $a_{\mathrm{H}}{}^{\beta} \leqslant 3.0$ Oe.[8,17–20,23] Dilution of alcohol with benzene decreases a_{N} just as predicted in ref. 24 (Table 2). [According to ref. 23 in pure toluene the a_{N} value of $(\mathrm{A_1{}^{\bullet}})$ is 0.1—0.3 Oe smaller than in the alcohol corresponding to the trapped radical.] Whenever only one of the two radicals $(\mathrm{A_1{}^{\bullet}})$ or $(\mathrm{A_2{}^{\bullet}})$ was formed its identification was verified by the following simple test: if introduction of atmospheric oxygen left the spin-adduct yield almost unaffected, it was radical $(\mathrm{A_2{}^{\bullet}})$; if, on the other hand, no spin-adduct was formed on introduction of atmospheric oxygen, it was radical $(\mathrm{A_1{}^{\bullet}})$, since it is known that in air-saturated solutions $\mathrm{R^1R^2\dot{C}OH}$ radicals are rapidly converted into peroxyl radicals and are not accepted by PBN.[16]

In a number of cases the e.s.r. spectra of radical $(\mathrm{A_3{}^{\bullet}})$ (Table 2) were recorded apart from those of radicals $(\mathrm{A_1{}^{\bullet}})$ and $(\mathrm{A_2{}^{\bullet}})$. The PsO$^{\bullet}$ radicals are present in an excess relative to $(\mathrm{A_1{}^{\bullet}})$ or $(\mathrm{A_2{}^{\bullet}})$, so that reactions (13) and (14), where R$^{\bullet}$ is the alcohol radical, may take place in solution.



$$\mathrm{C_6H_5\underset{\substack{|\\R}}{C}H-\underset{\substack{|\\O^{\bullet}}}{N}-C(CH_3)_3 + PsO^{\bullet} \longrightarrow C_6H_5\underset{\substack{|\\R}}{C}=\underset{\substack{\downarrow\\O}}{N}-C(CH_3)_3 + PsOH} \qquad (13)$$



$$\mathrm{C_6H_5-\underset{\substack{|\\R}}{C}=\underset{\substack{\downarrow\\O}}{N}-C(CH_3)_3 + R^{\bullet} \longrightarrow C_6H_5-\overset{R}{\underset{\substack{|\\R}}{C}}-\underset{\substack{|\\O^{\bullet}}}{N}-C(CH_3)_3} \qquad (14)$$

The fact that the amount of $(\mathrm{A_2{}^{\bullet}})$ formed during oxidation of Bu^{t}OH (Table 2) is small is apparently due to the fact that reaction (9) involving participation of Bu^{t}O$^{\bullet}$ does not totally prevail over other routes of decay of this radical (recombination, decomposition, abstraction of hydrogen atom from the solvent molecule[25]).

Thus it follows from Table 2 that oxidation of alcohol at 373 K occurs, in the general case, *via* two competing mechanisms (A) and (B). The secondary alcohols which have weaker α-C–H bonds are predominantly oxidized by way of hydrogen abstraction. Normal alcohols and Bu^{t}OH are predominantly oxidized by way of electron transfer. When the temperature is lowered from 373 to 338 K, the two radical species $(\mathrm{A_1{}^{\bullet}})$ and $(\mathrm{A_2{}^{\bullet}})$ are not formed simultaneously. The radical which was preferably formed at 373 K is the only one produced at 338 K. Thus, as usual, lowering the temperature enhances the selectivity. When a different solvent is used, *e.g.*, $\mathrm{C_6H_6}$ containing 5% by volume of $\mathrm{R^1R^2CHOH}$ instead of pure $\mathrm{R^1R^2CHOH}$, the reaction mechanism remains the same (Table 2). Unlike many reactions of hydrogen abstraction (electron transfer) from alcohols by active radicals such as OH$^{\bullet}$, H$^{\bullet}$, $\mathrm{SO_4{}^{-\bullet}}$, $\mathrm{{}^{\bullet}H_2PO_4}$, and $\mathrm{{}^{\bullet}CCl_3}$, investigated earlier, reaction (1) is more than 10 orders of magnitude slower. The reactions are characterized both by low *A* values and high E_{a} values (Table 1). The apparent steric hindrances in the transition state of reaction (1) are responsible for the low *A* values. Similarly, low values of *A*, *ca.* 10^2—10^6 l mol^{-1} s^{-1}, were obtained in ref. 4 for hydrogen-abstraction reactions from phenols and hydrocarbons by stable 2,6-di-t-butyl-substituted aroxyl radicals. G$^{\bullet}$ is a more sterically hindered compound than PsO$^{\bullet}$; therefore, the value of *A* for reaction (1) of Pr^{n}OH oxidation by G$^{\bullet}$ radicals is 10^3 times smaller than that for the same reaction involving PsO$^{\bullet}$ (Table 1).

Obviously there is no correlation between E_{a} and *D*(C–H) in alcohols for reaction (1) that can take two routes (the solvent effect on E_{a} may be considered to be weak) (Table 1). (A correlation of this sort has been observed in ref. 26, for example, for hydrogen-atom abstraction by $\mathrm{{}^{\bullet}CCl_3}$ radicals.)

An increase of $\mathrm{R^1R^2CHOH}$ concentration in $\mathrm{C_6H_6}$ results in an increase of the proportion of radicals combined into hydrogen-bond complexes $\mathrm{PsO^{\bullet}\cdots HOCHR^2R^1}$ and at the same time deceleration of reaction (1) (Table 1). This provides further evidence in favour of the fact that oxidation of alcohols does not involve hydrogen-atom abstraction from the O–H bond, since the formation of hydrogen-bond complexes with the help of the abstracted hydrogen atom should accelerate reaction.[6] Complexes are, of course, less reactive both in the reaction of hydrogen-atom abstraction from the α-C–H bond of the free alcohol molecule and in the electron-transfer reaction from the free alcohol molecule. The formation of complexes between the reactants and the surrounding dipole molecules increases the solvent reorganization energy and inhibits the electron-transfer process.[25]

When $\mathrm{CH_3OD}$ is used instead of $\mathrm{CH_3OH}$, the rate of reaction (1) is practically unchanged (Table 1). However, when $\mathrm{CD_3OD}$ is used in place of $\mathrm{CH_3OH}$ ($\mathrm{CH_3OD}$), $k_{\mathrm{H}}/k_{\mathrm{D}} = 2.7 \pm 0.8$

(Table 1) which might be interpreted as an isotope effect for hydrogen-atom abstraction from the α-C–H bond. However, in this particular case we 'diagnosed' electron transfer (Table 2). Similarly, the authors of ref. 8 have shown that the oxidation of CH_3OH with the strongest oxidant, $SO_4^{-\bullet}$ radical, occurs *via* electron-transfer, and the authors of ref. 7 have shown for the same reaction in experiments with deuteriated alcohols that k_H/k_D also equals 2.7 and concluded that $SO_4^{-\bullet}$ abstracts the α-hydrogen-atom from CH_3OH and other alcohols. Our opinion is that there is no contradiction between the data of ref. 7 and 8 and the results of the present work: oxidation of CH_3OH with $SO_4^{-\bullet}$ and $PsO^{\bullet}$ occurs predominantly *via* electron transfer, whereas the deuteriated alcohol CD_3OD probably has a higher oxidation potential. It is known in fact that deuterium substitution usually leads to a slight increase of ionization potential (I.P.) of organic compounds. Besides, the electron-transfer reaction rate is controlled not only by the reaction enthalpy or free energy but also by the solvent reorganization energy and bond reorganization energy or internal reorganization energy (see, *e.g.*, ref. 3). The last quantity should be higher for the deuterium-substituted compound and should thus cause a decrease of the electron-transfer rate constant. It has to be noted, besides, that the measured values of the isotope effect (2.7) are small compared with the value of *ca.* 10 usual for the homolytic hydrogen-abstraction reactions.[28] Acceleration of aroxyl decay in the presence of PBN was observed only in normal alcohols which react by electron transfer. Apparently, PBN stimulates electron transfer in the complex [reaction (15)].

$$\begin{aligned}&\mathrm{PsO^{\bullet}\cdots HOCHR^2R^1 + PBN} \rightleftharpoons\\&\qquad \mathrm{PsO^{\bullet}\cdots HO\overset{\bullet +}{C}HR^2R^1 + PBN^{-\bullet}} \longrightarrow\\&\qquad\qquad \mathrm{PsOH + R^1R^2CHO^{\bullet} + PBN} \quad (15)\end{aligned}$$

We do not believe that the rate constants of the reactions between aroxyl radicals and alcohols in the presence of PBN (Table 1) are elementary ones because the reaction mechanism is too complex [reactions (1), (13), and (15)]. It is known that nitroxyl radicals are able to take part in electron-transfer reactions with aroxyl radicals and thereby promote their decay.[2] Nevertheless, addition of PBN to aroxyl solutions did increase the radical decay rate right from the beginning of the reaction, which proves the participation of PBN in the process [reaction (15)].

As follows from the data of Table 1, DSTDP reduces $PsO^{\bullet}$ at 388 K more effectively than R^1R^2CHOH. It is clear why DSTDP is used as a synergist with the corresponding phenol as inhibitor.[5] Reaction (5) may involve electron transfer from the DSTDP molecule due to the presence of a nucleophilic sulphur atom in the DSTDP molecule, or abstraction of α- or β-hydrogen atoms activated by the neighbouring groups. The radicals formed from DSTDP cannot, unfortunately, be trapped by PBN and, therefore, it was impossible to establish the mechanism of the elementary reaction.

Conclusions.—Unlike a number of other compounds with labile hydrogens, *e.g.* amines, alcohols possess a remarkable ability to form different radicals when reacting *via* hydrogen abstraction or electron transfer, and the $PsO^{\bullet}$ radical does not trap the resultant alcohol radicals. These two features have permitted us to establish the mechanism of reaction (1) which was carried out in the presence of a spin trap.

Rate constants of the slow elementary reactions of aliphatic alcohol oxidation by aroxyl radicals have been obtained. At 373 K the reaction follows two competing routes: electron transfer and hydrogen-atom abstraction. The latter reaction path is favoured by low D(C–H) values and the former by the low oxidation potentials of alcohols (which may only very roughly be represented by I.P.). When the temperature is lowered to 338 K, the reaction becomes selective: normal alcohols are oxidized *via* electron transfer and secondary ones *via* hydrogen-atom abstraction.

It is often assumed that a reaction of type (1A) involves complex formation with a certain degree of charge separation.[1,2,9,15] However, speculation of this kind does not in any way allow mechanisms (A) and (B) to be continued, since the products of the elementary reactions (A) and (B) are different. The cumulative data show that in many cases hydrogen- and electron-transfer are competing or independent processes.[29,30]

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