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Kinetics of the reaction of the TEMPO radical with alkylarenes

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The kinetics of the reaction of the stable radical 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) with a series of alkylarenes containing primary and secondary benzyl C—H bonds was studied by ESR, and the reaction rate constants were determined. The scheme of the process under study was examined, and the applicability boundaries of the simplification during analysis were shown. The selectivities of TEMPO and the more reactive cumylperoxyl radical were compared.

Key words: TEMPO radical, alkylarenes, kinetics, computer simulation, rate constants of hydrogen atom abstraction.

Homolytic reactions involving stable radicals are studied from the point of view of the inhibition effect of these radicals in chain-radical oxidation[1—4] and their important role in processes of so-called "living" polymerization.[5—7] The reactions of H atom abstraction from hydrocarbon molecules by O-centered alkoxy and peroxy radicals have been studied to presently in detail.[8—11] Data on H atom abstraction by the least active radicals among the O-centered radicals, *viz.*, *N*-oxide radicals, are much more limited.

The purpose of this work is to study the kinetics of the reactions of the stable 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO) with alkylarenes (RH) containing the primary and secondary benzyl C—H bonds and to evaluate how the reversibility of particular steps of the reaction of RH with TEMPO influences the consumption rate of the latter. Alkylarenes were chosen as substrates because they are characterized by a wide interval of dissociation energies of the benzyl C—H bonds: xylenes, mesitylene, pseudocumene, durene, hexamethylbenzene, *p*-diethylbenzene, fluorene, diphenylmethane, acenaphthene, octahydroanthracene, dodecahydrotriphenylene, and dihydroanthracene.

Experimental

Liquid hydrocarbons were purified using a previously described procedure.[12] Solid hydrocarbons were recrystallized from EtOH. *tert*-Butylbenzene, which was also purified using a known procedure,[12] was used as the solvent. The reaction kinetics was studied by measuring the changes in the concentration of the stable radical using ESR as described previously.[13] ESR spectra were recorded with a 3-cm Radiopan SE/X-2544 spectrometer using Mn^{2+}/MgO as an internal standard. The reaction was carried out in an inert atmosphere in sealed glass tubes placed in a thermostat. Oxygen was removed from the samples by evacuation upon freezing the solutions in liquid nitrogen followed by saturation with argon. The reaction temperature changed within 105—155 °C and was maintained constant with an accuracy of ±0.5 °C. The initial concentrations of TEMPO were $\sim 10^{-4}$ mol L^{-1}. In the case of liquid alkylarenes, kinetic experiments were carried out in a substrate medium. The concentration of alkylarenes was selected in such a way that the half-life of TEMPO would be 0.5—7.0 h. Preliminary experiments showed that TEMPO was not consumed in pure *tert*-butylbenzene for 7 h at 135 °C (the most part of measurements was performed at this temperature).

The direct kinetic problem was solved using the specially developed program in which the solution of a system of rigid differential equations was solved by the Euler and Gear methods. Quantum-chemical calculations were performed using the MOPAC program package.[14]

Results and Discussion

The experimental measurements of the changes in the TEMPO concentration in time showed that the stable radical was intensely consumed in solutions of the alkylarenes under study in the 105—155 °C temperature interval. Since the concentration of alkylarenes is by several orders of magnitude higher than that of TEMPO, the kinetic curves are well linearized in the $\ln(I/I_0)$—t coordinates (Fig. 1), where I and I_0 are the intensities of the ESR signals of the sample and reference, respectively; t is time. The apparent rate constants of TEMPO consumption in the reaction with alkylarenes (k_{app}), which were obtained from these plots, range from 10^{-6} to 10^{-5} s^{-1} (Table 1) and change proportionally to the substrate concentration, *i.e.*, the reaction order with respect to the substrate is equal to 1.

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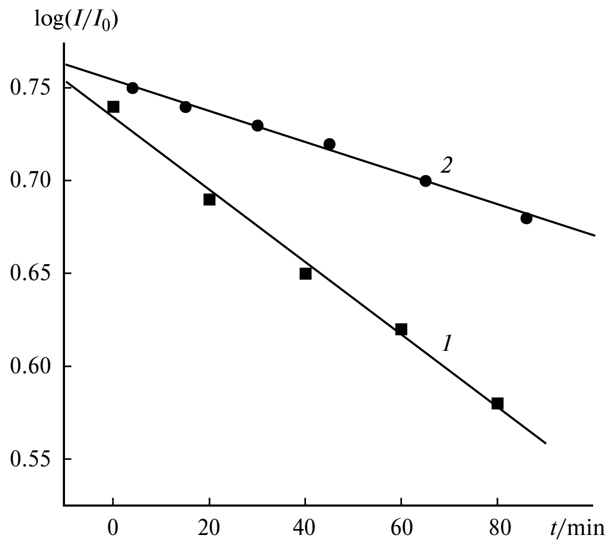


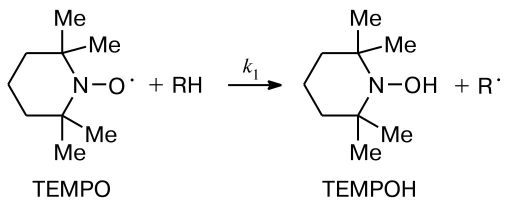
Fig. 1. Logarithmic anamorphoses of the kinetic curves of TEMPO consumption in the reactions with *p*-diethylbenzene (*1*) and diphenylmethane (*2*) at 135 °C.

Table 1. Rate constants of the reactions of TEMPO with hydrocarbons (RH) at 135 °C

RH	[RH] /mol L^{-1}	$k_{app} \cdot 10^5$ /s^{-1}	k_1 /L mol^{-1} s^{-1}
o-Xylene (**1**)	8.30	1.7±0.22	$(1.0\pm0.13)\cdot10^{-6}$
m-Xylene (**2**)	8.18	1.6±0.02	$(0.96\pm0.01)\cdot10^{-6}$
p-Xylene (**3**)	8.11	1.5±0.12	$(0.93\pm0.07)\cdot10^{-6}$
Mesitylene (**4**)	7.20	4.3±0.58	$(3.0\pm0.4)\cdot10^{-6}$
Pseudocumene (**5**)	7.29	3.1±0.34	$(2.1\pm0.2)\cdot10^{-6}$
Durene (**6**)	1.00	0.99±0.06	$(4.9\pm0.3)\cdot10^{-6}$
Hexamethylbenzene (**7**)	0.25	1.4±0.23	$(2.7\pm0.5)\cdot10^{-5}$
Diphenylmethane (**8**)	1.00	3.2±0.14	$(1.6\pm0.1)\cdot10^{-5}$
Acenaphthene (**9**)	0.50	4.6±0.39	$(4.6\pm0.4)\cdot10^{-5}$
Octahydroanthracene (**10**)	0.50	8.6±0.42	$(8.6\pm0.4)\cdot10^{-5}$
Dodecahydrotriphenylene (**11**)	0.13	5.9±0.73	$(2.3\pm0.3)\cdot10^{-4}$
Dihydroanthracene (**12**)	0.0056	14±0.67	$(1.2\pm0.1)\cdot10^{-2}$
Fluorene (**13**)	0.50	24±0.60	$(2.4\pm0.1)\cdot10^{-4}$
p-Diethylbenzene (**14**)	6.42	8.6±0.94	$(6.7\pm0.7)\cdot10^{-6}$

Taking into account the published[15—18] data, we can present the reaction of TEMPO with a hydrocarbon RH in the most general form by Scheme 1.

Scheme 1



(1)

$$\text{TEMPOH} + \text{R} \xrightarrow{k_{-1}} \text{TEMPO} + \text{RH} \qquad (2)$$

$$\text{TEMPO} + \text{R} \xrightarrow{k_2} \text{TEMPOR} \qquad (3)$$

$$\text{TEMPOR} \xrightarrow{k_{-2}} \text{TEMPO} + \text{R} \qquad (4)$$

$$\text{R} + \text{R} \xrightarrow{k_3} \text{RR} \qquad (5)$$

The contribution from each step to the kinetics of the process depends on the structure of R and temperature. Therefore, it was necessary to study the effect of each step in Scheme 1 on the kinetics of TEMPO consumption under our experimental conditions and thereby to show what is the apparent reaction rate constant (k_{app}) determined using the equation of the first order. Since the kinetic equations corresponding to the complete Scheme 1 cannot be obtained in the integral form, the mathematical simulation method was chosen to analyze this scheme. In order to apply successfully this method, one has to estimate the boundaries of probable variation of the rate constant values for each of the steps and to choose a reliable method of integration of the resulting system of differential equations.

The data on the k_2 values obtained at 294—298 K are available[15,16]: k_2 ~10^7—10^9 L mol^{-1} s^{-1}. Taking into account the low activation energies of this reaction and the higher temperature of the reaction in our experiments (408 K), we can assume that the k_2 values range within 10^8—10^9 L mol^{-1} s^{-1}. The k_3 values change[15] from 10^7 to 10^9 L mol^{-1} s^{-1}. We have no data on the k_{-1} values for our systems. However, the rate constants of similar reactions leading to other O-centered stable radicals (phenoxyls) are known.[19,20] The rate constants of the reactions of phenols with alkyl radicals are[19,20] ~10—10^2 and ~10^3—10^4 L mol^{-1} s^{-1} for the vinyl acetate and methyl radicals, respectively. This constant for the *N*-phenyl-*N*-alkylhydroxylamine is[21] $1.8\cdot10^4$ L mol^{-1} s^{-1}.

We found no published k_{-2} values for TEMPOR which is of interest for us (see Scheme 1, reaction (4)). Therefore, the k_{-2} value was estimated from the correlation of the dissociation energy of the cleaved C—O bond (E_{C-O}) in *N*-alkoxyamines (TEMPOR) with the rate constants of their decomposition. Since E_{C-O} for the reactions of TEMPO with radicals of the alkylarenes under study are unknown, we used the semiempirical quantum-chemical PM3 method for their calculation. This method provides the thermodynamic characteristics closest to experimental values for molecular species containing C, H, O, and N atoms.[14] The energy of the molecule was calculated in the framework of the restricted Hartree—Fock method with full optimization of all geometrical parameters. For comparison of the calculated and experimental data, we took the enthalpy[18] ΔH_{-2} of the reaction of the radical formed from Ph_2CHMe with 4-hydroxy-TEMPO accepted as E_{C-O} and the known[17] E_{C-O} values of alkoxyamines for the following alkyl radicals R: Me, $PhCH_2$, PhCHMe, and $PhCMe_2$. We obtained a satisfactory (with the correlation coefficient 0.98) linear correlation between the experimental values $(E_{C-O})_{exp}$ and the results of quantum-chemical calculations $(E_{C-O})_{calc}$

$$(E_{C-O})_{exp} = (19.9\pm1.6) + (0.67\pm0.07)(E_{C-O})_{calc}. \quad (6)$$

This equation made it possible to estimate the dissociation energy of the C—O bond in the TEMPOR compounds formed in the reactions of the alkylarenes under study: 33, 32, 31, and 32.6 kcal mol^{-1} for xylene, durene, acenaphthene, and dodecahydrotriphenylene, respectively. The constants $K_2 = k_2/k_{-2}$ for the R radicals under study were calculated using the E_{C-O} values estimated from Eq. (6) as enthalpies ΔH_{-2}, and the entropy value was taken equal to ΔS_{-2} = 36 cal mol^{-1} K^{-1}, as for the reaction of the radical formed from Ph_2CHMe with 4-hydroxy-TEMPO.[18] This estimate gave the equilibrium constants K_2 of an order of 10^9—10^{10} L mol^{-1} and, hence, the k_{-2} value can range from 0.1 to 1 s^{-1}.

Thus, a probable interval of variation of the rate constants of particular steps in Scheme 1, considering the obtained estimates and experimentally measured apparent rate constants of TEMPO consumption (see Table 1), is the following: $k_1 = 10^{-6}$—10^{-4} L mol^{-1} s^{-1}; k_{-1} = 10—10^4 L mol^{-1} s^{-1}; $k_2 = 10^8$—10^9 L mol^{-1} s^{-1}; k_{-2} = 0.1—1 s^{-1}; $k_3 = 10^7$—10^9 L mol^{-1} s^{-1}. Since the interval of rate constants is 10^{-6}—10^9, the system of differential equations corresponding to Scheme 1 is stiff. We chose two most often used methods of numerical integration of such systems: Gear method and implicit Euler method. We compared the results of calculations obtained by these methods in order to check the validity of the solution. The results, identical with the accuracy to four significant digits, were obtained for the system of differential equations that takes into account all steps. The complete coincidence of the results of numerical integration and calculation by algebraic equations was obtained for the simplified scheme (see Scheme 1, reactions (1), (2), and (3)) with integral equations. The Gear method was used in subsequent calculations.

The most important particular cases of the proposed scheme were examined in more detail: (1) contribution of the fluxes with k_{-1} and k_{-2} is insignificant; (2) contribution of the flux with k_{-2} is insignificant; (3) contribution of the flux with k_{-1} is insignificant; (4) all five steps are important.

Case 1. The numerical integration of the system of differential equations ignoring the flows with k_{-1} and k_{-2} at the rate constants $k_1 = 5 \cdot 10^{-6}$—$5 \cdot 10^{-4}$ L mol^{-1} s^{-1}, $k_2 = 1 \cdot 10^9$ L mol^{-1} s^{-1}, $k_3 = 1 \cdot 10^8$ L mol^{-1} s^{-1}, and [TEMPO] = $1 \cdot 10^{-4}$ mol L^{-1}, [RH] = 1 mol L^{-1} using the Gear method showed that [TEMPO] >> [R]. For example, at [TEMPO] ≈ 10^{-5} mol L^{-1} and $k_1 = 5 \cdot 10^{-4}$ L mol^{-1} s^{-1} the ratio of fluxes (2) and (5) is ~10^{10}. In this case, flux (5) can be neglected, and the equation for the consumption rate of TEMPO takes the form

$$-d[TEMPO]/dt = 2k_1[TEMPO][RH].$$

At [TEMPO] << [RH] the apparent rate constant is

$$k_{app} = 2k_1[RH]. \quad (7)$$

Case 2. When the first step is equilibrium, the scheme of the reaction includes Eqs. (1), (2), and (3). When the contribution of reaction (5) is small (this is indirectly confirmed by the published data[3]), the following expression can be written for the consumption of TEMPO:

$$d[TEMPO]/dt = -k_1[TEMPO][RH] - k_2[TEMPO][R] + k_{-1}[TEMPOH][R].$$

Taking into account the condition of stationarity, we can write

$$-d[TEMPO]/dt = 2Bk_1[TEMPO][RH], \quad (8)$$

where $B = 1 - [1/(k_2[TEMPO]/k_{-1}[TEMPOH]) + 1)]$.

The B coefficient depends on the ratio $k_2[TEMPO]/k_{-1}[TEMPOH] = A$: if it is high, the B coefficient is equal to 1 and then k_{app} is described by Eq. (7). Thus, the A value is a criterion of the accuracy of Eq. (7). Comparing the values of particular fluxes before the achievement of the half-life when [TEMPO] ≈ [TEMPOH], we can conclude that at $k_2/k_{-1} \gg 1$ Eq. (7) is exact. This is valid in our case: at the lowest k_2 values (10^7 L mol^{-1} s^{-1}) and the highest k_{-1} values (10^{-4} L mol^{-1} s^{-1}), k_2/k_{-1} is ~10^3. At high degrees of conversion of TEMPO, the inequality $A \gg 1$ is not fulfilled.

The boundary values for the rate constants k_1, k_2, and k_{-1}, when the process can be described by the simplified scheme including only reactions (1) and (2), were determined as follows: the kinetic curves were calculated before the achievement of the half-life time of TEMPO while keeping the k_1 value unchanged and varying k_2 (10^7—10^9 L mol^{-1} s^{-1}) and k_{-1} (0—$2 \cdot 10^9$ L mol^{-1} s^{-1}). The k_2 and k_{-1} values at which the difference in the TEMPO concentrations calculated taking into account and ignoring flux (2) did not exceed 5% were considered boundary. It is established that the boundary of the region, where flux (2) can be neglected, is a straight line in the $\log k_2$—$\log k_{-1}$ coordinates regardless of the k_1 value, and the kinetics is described by the simplified scheme at $\log k_2 - \log k_{-1} > 2$. The qualitative criterion of the role of step (2) in the kinetics of TEMPO consumption can be determined. The numerical simulation shows that the shape of the kinetic curve presented in the $\log([TEMPO]/[TEMPO]_0)$—t coordinates depends on the

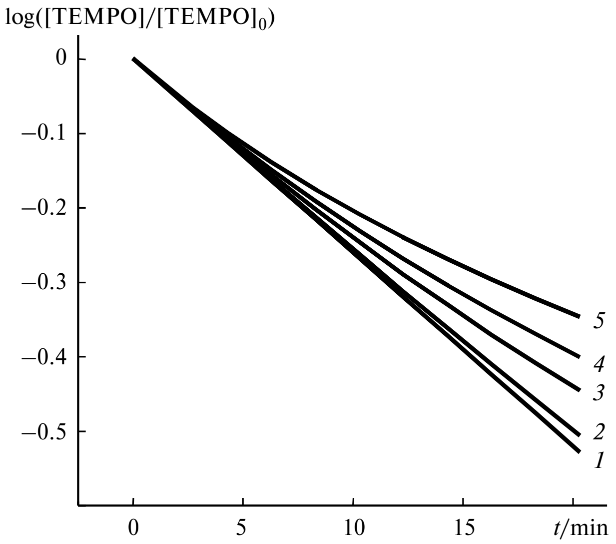


Fig. 2. Plots of log([TEMPO]/[TEMPO]$_0$) *vs.* time for $k_2 = 1 \cdot 10^9$ L mol^{-1} s^{-1} and $k_1 = 5 \cdot 10^{-4}$ L mol^{-1} s^{-1} at different k_{-1} values: 0—$5 \cdot 10^7$ (*1*), $1 \cdot 10^8$ (*2*), $5 \cdot 10^8$ (*3*), $1 \cdot 10^9$ (*4*), and $2 \cdot 10^9$ L mol^{-1} s^{-1} (*5*).

k_2/k_{-1} ratio (Fig. 2). When the efficiency of the inverse reaction (2) increases for $k_1 = 5 \cdot 10^{-4}$ L mol^{-1} s^{-1}, $k_2 = 1 \cdot 10^9$ L mol^{-1} s^{-1}, and $k_{-1} > 5 \cdot 10^8$ L mol^{-1} s^{-1}, no linear plot of log[TEMPO]/[TEMPO]$_0$ *vs.* t is observed, and the deviation from linearity in these coordinates can be considered as a proof of the substantial role of this process. In all cases, the obtained experimental data were well linearized in the ln$I$—t coordinates, indicating a small contribution of reaction (2).

Case 3 (only steps of chain termination are equilibrium, *i.e.*, reactions (1), (3), (4), and (5) are considered). The reversibility of this step, in particular, plays a substantial role in the reaction of TEMPO with alkyl radicals during polymerization of some vinyl monomers.[3,4] The influence of the K_2 value on k_{app} was analyzed for the model. The results of calculations show that the k_{app} values remain unchanged with changing $k_{-2} = 10$—$1 \cdot 10^9$ s^{-1} and $k_2 = 1 \cdot 10^7$—$1 \cdot 10^9$ L mol^{-1} s^{-1}. The deviation of k_{app} greater than 5% is observed for $k_1 = 5 \cdot 10^{-6}$ L mol^{-1} s^{-1} and $k_2 = 1 \cdot 10^9$ L mol^{-1} s^{-1} at $K_2 < 1 \cdot 10^6$ L mol^{-1}, while for $k_1 = 5 \cdot 10^{-4}$ L mol^{-1} s^{-1} and $k_2 = 1 \cdot 10^9$ L mol^{-1} s^{-1} it is observed at $K_2 < 1 \cdot 10^7$ L mol^{-1}. According to the estimation of the kinetic parameters in the reaction scheme under study, the K_2 values are of an order of 10^9—10^{10} L mol^{-1} and, hence, the reversibility of the chain termination step can be neglected.

Case 4 (complete scheme with equilibria in the first and second steps and recombination of alkyl radicals). We calculated the kinetics of TEMPO consumption using the Gear method and considering all steps. The average of the values measured in our series was used: $k_1 = 5 \cdot 10^{-5}$ L mol^{-1} s^{-1}. The maximum k_{-1} value was taken in the possible interval of its changes: $1 \cdot 10^4$ L mol^{-1} s^{-1}. The data obtained (Table 2) show that in the whole interval of changes of other kinetic parameters, the deviations of the TEMPO concentrations calculated from the scheme including only reactions (1) and (3) do not exceed 2.5%. Thus, variant (1) of Scheme 1 can be accepted with a satisfactory accuracy for describing the kinetics in this case. The calculations show that the discrepancy between the kinetic curves, which were described by the simplified scheme (considering only reactions (1) and (3)) and all other schemes, increases substantially with an increase in the degree of conversion of the stable radical, and the plot of log([TEMPO]/[TEMPO]$_0$) *vs.* t becomes nonlinear. According to our analysis, the optimum method for the exact determination of k_1 even at a substantial contribution of reactions (2), (4), and (5) can be the extrapolation of the slope ratio of the line drawn in the log([TEMPO]/[TEMPO]$_0$)—t coordinates to the initial time. We did not observe deviations from linearity when the kinetic data were presented in these coordinates, which can additionally provide evidence in favor of an insignificant role of steps (2), (4), and (5) under our experimental conditions.

Table 2. Difference (Δ) between the concentrations of TEMPO in its half-life calculated according to the scheme taking into account only reactions (1) and (3) and according to the scheme including all five reactions in Scheme 1*

k_{-2}/s^{-1}	k_3	k_2	Δ (%)
	L mol^{-1} s^{-1}		
0.001	$1 \cdot 10^9$	$1 \cdot 10^9$	0.001
0.001	$1 \cdot 10^9$	$1 \cdot 10^8$	0.011
0.001	$1 \cdot 10^7$	$1 \cdot 10^9$	0.001
0.001	$1 \cdot 10^7$	$1 \cdot 10^8$	0.011
0.010	$1 \cdot 10^9$	$1 \cdot 10^9$	0.010
0.010	$1 \cdot 10^9$	$1 \cdot 10^8$	0.115
0.010	$1 \cdot 10^7$	$1 \cdot 10^9$	0.010
0.010	$1 \cdot 10^7$	$1 \cdot 10^8$	0.098
0.100	$1 \cdot 10^9$	$1 \cdot 10^9$	0.114
0.100	$1 \cdot 10^9$	$1 \cdot 10^8$	2.49
0.100	$1 \cdot 10^7$	$1 \cdot 10^9$	0.097
0.100	$1 \cdot 10^7$	$1 \cdot 10^8$	0.967

* The calculations were carried out with variation of the k_2, k_{-2}, and k_3 constants while keeping unchanged $k_1 = 5 \cdot 10^{-5}$ L mol^{-1} s^{-1}, $k_{-1} = 1 \cdot 10^4$ L mol^{-1} s^{-1}, and an initial TEMPO concentration of $1 \cdot 10^{-4}$ mol L^{-1}.

Taking into account the above results, we can simplify Scheme 1 proposed for the reaction of the stable TEMPO radical with alkylarenes to two equations (1) and (3) and calculate the k_1 rate constants using Eq. (7).

Let us compare the rate constants obtained for the reactions of H atom abstraction by the TEMPO radical with the rate constants of H atom abstraction by the more

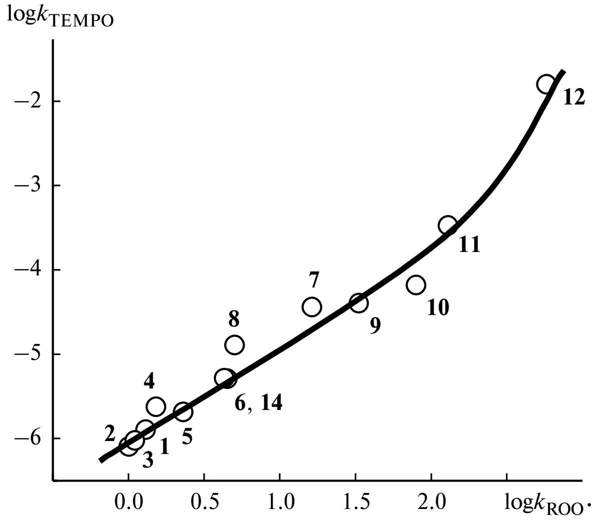


Fig. 3. Correlation between the rate constants of the reaction with alkylarenes **1—12** and **14** for the TEMPO (k_{TEMPO}) and peroxy radicals ($k_{\text{ROO}^\cdot}$).

reactive O-centered cumylperoxyl radical (ROO$^\bullet$).[8—11] The k_{TEMPO}(135 °C) values are by five orders of magnitude lower than $k_{\text{ROO}^\cdot}$(75 °C) for the reaction with the same hydrocarbons. This could be expected considering the difference between the energies of the formed O—H bond: it is ~70 kcal mol^{-1} for TEMPOH and about 90 kcal mol^{-1} for ROOH. The ratio between the logarithms of the reaction rate constants of the radicals under study is presented in Fig. 3. These data show a satisfactory, in general, correlation of these values, considering that the difference in temperatures at which the constants were measured was 60 °C. It is of interest that the slope ratio of the plot of logk_{TEMPO} *vs.* log$k_{\text{ROO}^\cdot}$ for the less reactive substrates is close to 1, although the radicals differ strongly in reactivity. This is explained by a significant difference in temperatures at which the constants were measured. The temperature increase suppresses substantially the selectivity of ROO$^\bullet$ in H atom abstraction reactions. Note that the difference in the selectivity of the action of RNO$^\bullet$ and ROO$^\bullet$ increases with an increase in the reactivity of the substrate. For example, for less reactive hydrocarbons **1—10** (see Table 1)

$$(\log k_{\mathbf{2}} - \log k_{\mathbf{10}})_{\text{RNO}^\cdot}/(\log k_{\mathbf{2}} - \log k_{\mathbf{10}})_{\text{ROO}^\cdot} \approx 1.03,$$

and for more reactive molecules **11** and **12** (see Table 1)

$$(\log k_{\mathbf{10}} - \log k_{\mathbf{12}})_{\text{RNO}^\cdot}/(\log k_{\mathbf{10}} - \log k_{\mathbf{12}})_{\text{ROO}^\cdot} \approx 2.5.$$

This can be explained by the fact that for the reactions of alkylarenes with ROO$^\bullet$ the transition state in the reaction coordinate is closer to the reactants, while for the reaction with RNO$^\bullet$ it is closer to the products. This assumption agrees with both the difference in the rate constant values and the observed changes in the selectivity.

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