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# Leveling of reactivity for intramolecular radical substitution reactions in viscous media

***R. R. Rakhimov,[a]* A. I. Prokof'ev,[b] and Ya. S. Lebedev[a]***

[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,*
*4 ul. Kosygina, 117977 Moscow, Russian Federation.*
*Fax: +7 (095) 938 2156*
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
*28 ul. Vavilova, 117813 Moscow, Russian Federation.*
*Fax: +7 (095) 135 5085*

A leveling of the reactivity was found for intramolecular radical reactions in substituted 2-oxyphenoxyls in viscous media. A comparison of rate constants in toluene, hexane, pentane, and vaseline oil shows that fast reactions are decelerated more rapidly than slow reactions.

**Key words**: reactivity, radicals, viscosity.

The effect of molecular mobility on chemical reactivity[1] and the leveling of chemical reactivity in comparison with the liquid phase[2] have been found for bimolecular radical substitution in polymers. In a qualitative sence, the leveling manifests itself in the fact that fast reactions are decelerated much more rapidly on going to the solid phase than slow reactions. The following empirical relationship is obeyed:

$$k_s \sim k_f{}^m, \qquad (1)$$

where $k_s$ and $k_f$ are rate constants of the reactions in the solid and in the liquid phase, respectively, and $m = 0.5 \div 1$ (see Ref. 2). In the present work, similar regularities for monomolecular reactions are reported for the first time.

It was previously shown[3] that intramolecular radical substitution in substituted 2-oxyphenoxyls is decelerated in viscous media, and the time of chemical exchange, $\tau_{ex} = 1/k$ ($k$ is the monomolecular rate constant), is proportional to the time of rotational correlation of the radicals, $\tau_c$. The data available can be semiquanitatively interpreted in the framework of the model of the indi-

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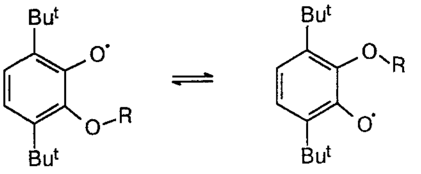
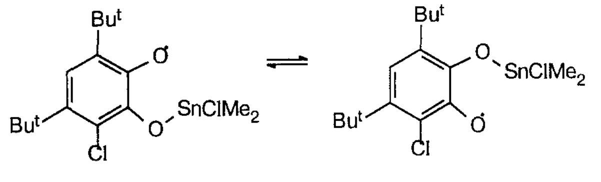
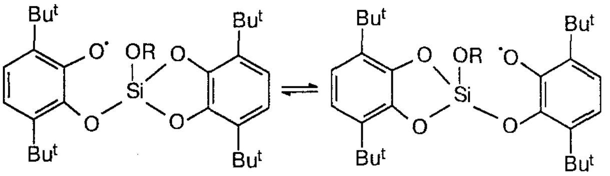
**Scheme 1**

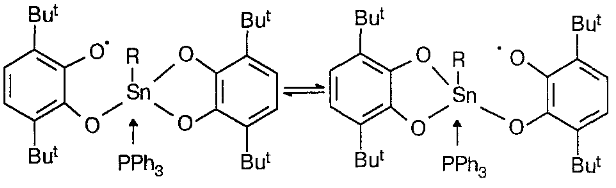


where R = $PbPh_3$ (**1**), ZnS(S)COBu(**2**), $SnClMe_2$(**3**)





RO = 4,6-di(*tert*-butyl)-2-oxidophenoxyl (**6**), 2,2,6,6-tetramethyl-4-oxidopiperidinoxyl (**7**),



R = 3,6-di(*tert*-butyl)-2-oxidophenoxyl (**8**).

rect cell effect.[3] The rate constant for the reaction in a viscous medium can be written in the following way:

$$1/k = 1/k_f + \alpha_0(\nu_0/k_f)^{1/2}\tau_c, \qquad (2)$$

where $\nu_0$ is the universal frequency factor and $\alpha_0$ is an empirical multiplier which takes into account the correlation between various types of molecular motion. Relationship (2) also describes the leveling of the reactivity. In the limiting case of highly viscous media (solid, $k_f \gg k$), relationship (1) with $m = 1/2$ follows from (2). However, at moderate viscosities, as Eq. (2) indicates, the effective $m$ value should increase, and for limiting nonviscous liquids, at $k \rightarrow k_f$, $m \rightarrow 1$.

The purpose of the present work was to find out whether leveling of the reactivity of 2-oxyphenoxyls occurs in intramolecular radical substitution (Scheme 1) using the known data on the rate constants of the reactions in various media.

Table 1 lists rate constants $k_f$ for reactions in nonviscous solvents (toluene, hexane, pentane) and those in vaseline oil, $k_{vo}$. As can be seen, fast intramolecular reactions slow down in a viscous medium more significantly than slow reactions. The dependence between $k_{vo}$ and $k_f$ presented in Fig. 1 indicates that the leveling effect may be described by relationship (1) with $m$ = 0.78 ± 0.07.

Obviously, this effect should be more pronounced when the rate constants in nonviscous solutions are compared with those in the solid state. However, the results obtained in the present work indicate that the

**Table 1.** Rate constants of intramolecular radical substitution reactions, $k_f$ and $k_{vo}$, at 20 °C

| Radical | $k_f/s^{-1}$ | $k_{vo}/s^{-1}$ | $k_f/k_{vo}$ | Reference |
|---|---|---|---|---|
| **1** | $7.7 \cdot 10^9$<br>(pentane) | $2.9 \cdot 10^8$ | 26.6 | 3,4 |
| **5** | $4.5 \cdot 10^9$<br>(toluene) | $2.7 \cdot 10^8$ | 16.7 | 5 |
| **2** | $2.0 \cdot 10^9$<br>(hexane) | $1.4 \cdot 10^8$ | 14.3 | 6 |
| **6** | $1.2 \cdot 10^9$<br>(toluene) | $1.1 \cdot 10^8$ | 10.9 | 5 |
| **7** | $1.0 \cdot 10^9$<br>(toluene) | $5.7 \cdot 10^7$ | 17.5 | 5 |
| **8** | $5.3 \cdot 10^8$<br>(toluene) | $3.6 \cdot 10^7$ | 14.7 | 3,7 |
| **4A** → **4B** | $3.7 \cdot 10^6$<br>(toluene) | $1.0 \cdot 10^6$ | 3.7 | 3 |
| **4B** → **4A** | $2.6 \cdot 10^6$<br>(hexane) | $6.7 \cdot 10^5$ | 3.9 | 3 |
| **3** | $1.7 \cdot 10^5$<br>(hexane) | $1.0 \cdot 10^5$ | 1.7 | 3 |

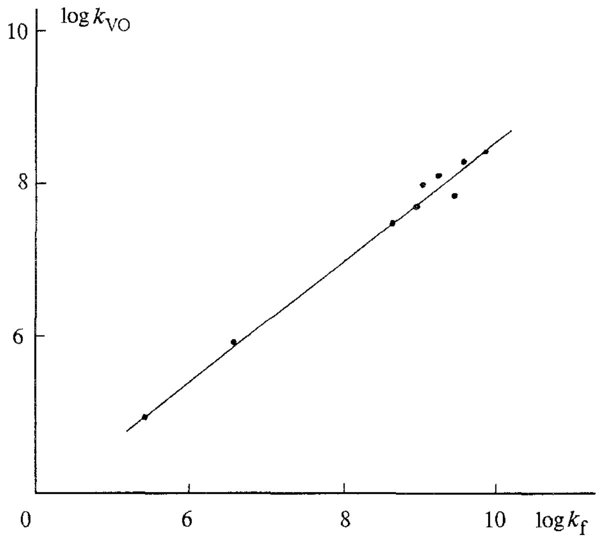


**Fig. 1.** The dependence between the rate constants of intramolecular radical reactions in vaseline oil, $k_{vo}$, and nonviscous liquids, $k_f$, at 20 °C.

leveling of the chemical reactivity can also be observed rather reliably on going from nonviscous solutions to viscous solutions at a temperature higher than the glass transition temperature of the solvent. This implies that the leveling effect should be taken into account in constructing theoretical models of liquid-phase intramolecular processes.

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## Experimental

The radicals studied in this work were prepared by the reaction of the corresponding organometallic derivatives with 3,6-di-*tert*-butylpyrocatechol in the presence of air followed by evacuation according to the previously described procedure.[4,7] Multiligand silicon-containing free radicals with pyrocatechol ligands were synthesized by the reaction of silicon bis-3,6-di-*tert*-butylpyrocatecholate with the corresponding radicals.[5] ESR spectra were recorded on a Varian E-12A spectrometer.

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# Structure and thermal stability of difluoroamino compounds in the liquid state

*V. N. Grebennikov,* G. B. Manelis, G. M. Nazin, and A. V. Fokin*

*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
*142432 Chernogolovka, Moscow Region, Russian Federation.*
*Fax: +7 (096) 515 3588*

The kinetics of decomposition of 15 difluoroamino compounds with $NF_2$ groups at primary, secondary, and tertiary carbon atoms in the liquid state was investigated. Activation energies ($E_a$) for all of the compounds were in the interval 100—120 $kJ \cdot mol^{-1}$. The reaction rate does not depend on the electronic effects of the substituents and decreases only in the case of steric shielding of the $NF_2$ group. For *N*-difluorobenzylamine it was shown that the gas-phase elimination of HF is characterized by $E$ = 176 $kJ \cdot mole^{-1}$, while the rate of decomposition in a solution depends on the dielectric constant of the medium. Based on the results obtained, a mechanism for liquid-phase decomposition, which involves heterolysis of the N—F bonds, is suggested.

**Key words:** difluoroamino compounds, thermal decomposition, reaction mechanism.

The most common type of organic compounds with an N—F bond are substances with $NF_2$ groups at the primary and secondary carbon atoms. Information on the thermal decomposition of these compounds is very limited. Some examples suggest that the gas-phase decomposition of these substances at moderate temperatures occurs as elimination of HF, and at higher temperatures (400—600 °C), the C—N bond cleaves.[1–3] For vicinal compounds, abstraction of $N_2F_4$ is also possible (see Ref. 4).

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