Correlation between solvent-reorganization dynamics and the kinetics of metallotropy in polar media

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

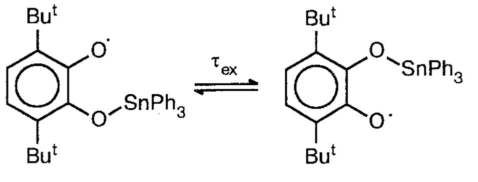
[a] N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences,
4 ul. Kosygina, 117977 Moscow, Russian Federation.
Fax: +7 (095) 938 2156
[b] A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, 117813 Moscow, Russian Federation.
Fax: +7 (095)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

The kinetics of metallotropy of the 3,6-di-*tert*-butyl-2-(triphenylstannyl)oxyphenoxyl radical has been studied by ESR. The correlation between chemical exchange time τ_{ex}, solvent polarity, and longitudinal relaxation time of the solvent corresponds to the model of a process controlled by molecular dynamics. A linear relation between τ_{ex} and correlation time τ_c for reorientation movements of the radical is found: $\tau_{ex} = \alpha \cdot \tau_c$. The coefficient α depends on the dielectric properties of the solvent.

Key words: kinetics; solvent dynamics; radical.

In recent years, some data on the effect of the molecular dynamics of a medium on the rates of intramolecular processes (chemical exchange reactions) has been obtained. It was shown that in general, there is a linear relationship between the characteristic time τ_{ex} of the exchange reactions and the rotational correlation time τ_c of the radical reagents in a medium:[1] $\tau_{ex} = \alpha \cdot \tau_c$.

As a rule, the dynamic properties of a medium (molecular mobility) can be modified by varying the viscosity of inert solvents (hexane, vaseline oil) and temperature. For the intramolecular radical transfer in 3,6-di-*tert*-butyl-2-(triphenylstannyl)oxyphenoxyl (radical **1**)



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(1)

and for the spin exchange in nitroxyl biradicals, a correlation between coefficient α and solvent polarity was disclosed.[2,3]

It is of interest to study the effect of the dielectric characteristics of a medium on the rates of intramolecular reactions and to examine the correlation between the kinetics of these reactions and the molecular dynamics taking into account solvent polarity. Now there are numerous data on the correlation between the molecular dynamics of a solvent and the kinetics of electron transfer in polar media.[4—9] In the framework of the solvent-reorganization models, the effect of the dielectric characteristics of the solvent manifests itself as a relation between the rate constant k and parameter $\gamma = (1/\varepsilon_{op} - 1/\varepsilon_s)$, where $\varepsilon_{op} = n^2$ is the optical dielectric constant, n is the refraction index, and ε_s is the statistical dielectric constant of a solvent. According to the well-known Marcus theory[10]

$$k = k_0 \exp\,[-(\Delta G_{is}{}^* + \Delta G_{os}{}^*)/RT], \tag{2}$$

where $\Delta G_{is}{}^*$ and $\Delta G_{os}{}^*$ are the reorganization energies of reagents ("intrasphere" reorganization) and of a polar medium ("intersphere" reorganization), respectively. The effect of solvent polarity on the rate constant is described by the following relation between $\Delta G_{os}{}^*$ and γ:[10]

$$\Delta G_{os}{}^* = \frac{\Delta Z^2 e^2 N}{4\pi\varepsilon_0}\left(\frac{1}{\bar{r}} - \frac{1}{d}\right)\gamma = B \cdot \gamma, \tag{3}$$

where e is the electron charge, ΔZ is the extent of charge transfer in the reaction, N is the Avogadro number, ε_0 is the dielectric constant in a vacuum, $\bar{r}$ is the mean molecular radius, and d is the distance of electron transfer.

The preexponential factor k_0 in the classic Marcus theory represents a simple collision factor for gas-phase reactions which is independent of the dynamic and polar characteristics of a medium. Taking into account the low sensitivity of $\Delta G_{is}{}^*$ to solvent polarity, Eq. (2) can be rearranged to the following form:

$$\ln k = A - B \cdot \gamma, \tag{4}$$

where $A = (\ln k_0 - \Delta G_{is}{}^*/RT)$ and B are constants (see

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Ref. 3). Although the dynamic characteristics of a medium may influence preexponential factor k_0 (see Ref. 11), relationship (4) remains correct for nonadiabatic processes. The preexponential factor for adiabatic electron transfer in polar media is dependent on the medium dynamics and inversely proportional to the longitudinal relaxation time τ_L of the solvent (relaxation time of a constant charge[12]):

$$k_0 \sim \tau_L^{-1}(\Delta G_{os}^*/RT)^{1/2}. \quad (5)$$

Then, instead of Eq. (4), one can obtain from Eqs. (2) and (5)

$$\ln(k\tau_L\gamma^{1/2}) = A' - B\gamma, \quad (6)$$

where A' is a constant.

One may expect that the rate constant for the intramolecular transfer of the metal fragment in radical **1** would be dependent on the solvent polarity, since the O—Sn bond in the radical is partially ionic.[13] Hence, it is of interest to study the relationship between the characteristic chemical exchange time τ_{ex} and the solvent relaxation time τ_L and to compare this relationship with the correlation between τ_{ex} and the characteristic rotational mobility time τ_c for the radical.

Experimental

Substituted 2-(stannyloxy)phenoxyl radicals were prepared by the interaction of the corresponding organotin derivatives with 3,6-di-*tert*-butylpyrocatechol in the presence of air followed by evacuation according to the earlier described procedure.[2] ESR spectra were recorded on a Varian E-12A instrument.

The method for deriving τ_{ex} and τ_c from ESR spectra of radical **1** has been described elsewhere.[14] Relaxation times τ_L for the solvents used were taken from Refs. 4, 15, 16.

Results and Discussion

Fig. 1 demonstrates the experimental dependences of τ_{ex} on τ_c for radical **1**. In agreement with our earlier findings,[14] they are linear ($\tau_{ex} = \alpha \cdot \tau_c$), and α decreases as the medium polarity increases. The α-values obtained are presented in Table 1. Using τ_{ex} measured for media with different dielectric characteristics, one can check the validity of Eqs. (4) and (6). Taking into account that k equals $1/\tau_{ex}$ for a monomolecular rate constant, Eqs. (4) and (6) can be rearranged to

$$\ln \tau_{ex} = -A + B\gamma \quad (7)$$

for the Marcus approach and to

$$\ln[(\tau_{ex}/\tau_L)\gamma^{1/2}] = -A' + B\gamma \quad (8)$$

for the model of chemical processes controlled by solvent relaxation.

Fig. 2 shows that the experimental dependence of τ_{ex} on γ for reaction (1) is inconsistent with the Marcus

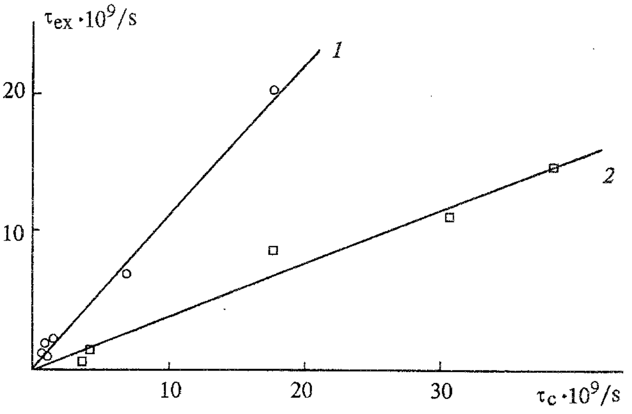

Fig. 1. τ_{ex} as a function of τ_c for radical **1** in CCl_4 (*1*) and DMSO (*2*).

Table 1. α-Values found for radical **1** and γ and τ_L for the solvents[4—15]

Solvent	α	T/K	γ(298 K)	γ($\bar{T}$)	$\tau_L \cdot 10^{12}$/s
CCl_4	1.1	240—300	0.022	0.023	3.08
Toluene	1.2	270	0.028	0.030	4.03
Bromobenzene	0.98	270	0.216	0.222	4.86
Chloroform	0.56	210—250	0.268	0.294	2.20
Pyridine	0.48	270	0.360	0.364	0.71
THF	0.61	230—280	0.372	0.381	0.81
DMSO	0.4	250—280	0.44	—	2.4

Note. The γ($\bar{T}$) values correspond to the mean temperature in the experiments and were calculated from literature data.[15]

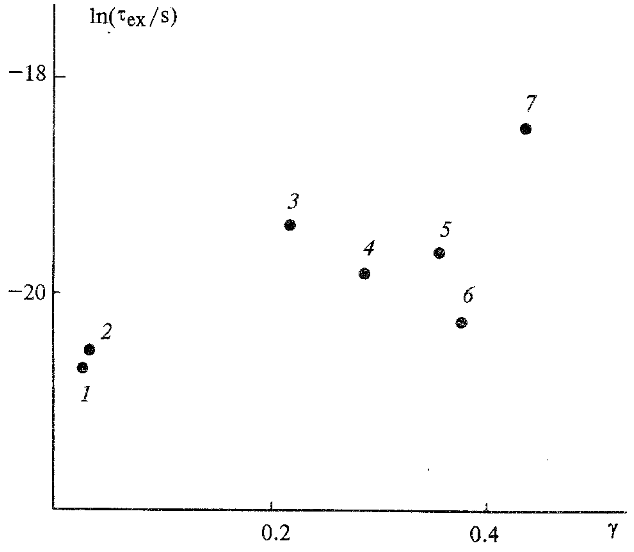

Fig. 2. ln τ_{ex} as a function of γ for reaction (1) in CCl_4 (*1*); toluene (*2*); bromobenzene (*3*); chloroform (*4*); pyridine (*5*); THF (*6*); DMSO (*7*).

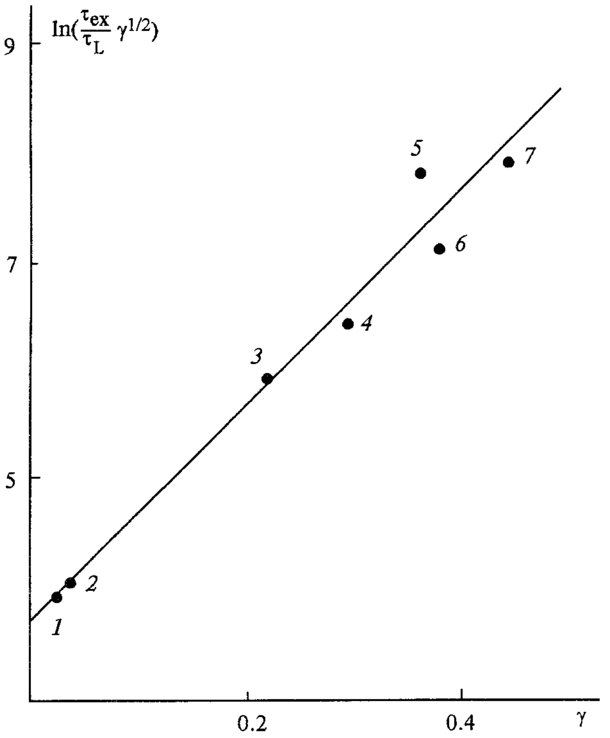

Fig. 3. τ_{ex} as a function of γ taking into account τ_L of the solvent according to Eq. (8).

approach. On the contrary, as seen from Fig. 3, the correlation between τ_{ex} and medium polarities is satisfactorily described in this case by Eq. (8), which takes into account the molecular dynamics of the solvent, *i.e.*, the dependence of τ_{ex} not only on γ, but also on τ_L. The validity of expression (8) can also be checked by substituting the α-values found for various solvents. Because α equals τ_{ex}/τ_c, a correlation between dynamic parameters τ_c and τ_L needs to be determined.

As follows from the spin-probe studies,[17] the frequencies of rotational and translational radical diffusion are generally proportional to each other:

$$\tau_c \sim \tau_D = 3V_M\eta/RT, \tag{9}$$

where τ_D is the Debye relaxation time, V_M is the molecular volume, and η is the solvent viscosity. Solvent longitudinal relaxation time τ_L and τ_D are related by the following equation:[12]

$$\tau_L = (\varepsilon_{op}/\varepsilon_s)\cdot\tau_D. \tag{10}$$

Then, one can obtain from Eqs. (8)—(10)

$$\ln\left(\alpha\frac{\varepsilon_s}{\varepsilon_{op}}\gamma^{1/2}\right) = C + B\gamma, \tag{11}$$

where C is a constant. As can be seen from Fig. 4, the correlation between α and γ is satisfactorily described by Eq. (11), *i.e.*, the relationship between the molecular

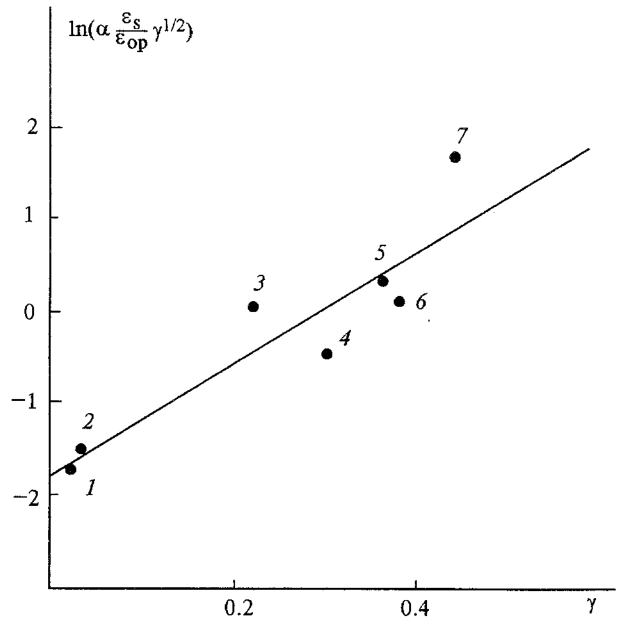

Fig. 4. α as a function of γ according to Eq. (11).

and chemical dynamics is governed by the dependence of the elementary rate constants on the rotational mobility of the reagents (parameter τ_c) or on the dielectric relaxation time τ_L of the solvent. Furthermore, coefficient α in the previously obtained correlation $\tau_{ex} = \alpha\cdot\tau_c$ allows for solvent polarity which is characterized by parameter γ.

Thus, the available data on the dependence of the kinetic parameters of intramolecular reactions on medium mobility are not in conflict with the solvent-reorganization models for electron transfer in polar media. However, these models cannot account for the leveling of reactivity found for bimolecular substitution reactions in polymers[18,19] and later for type (1) intramolecular processes in substituted 2-(R-oxy)phenoxyls.[20] Indeed, under conditions of unrestricted molecular mobility (in a free volume), when $\Delta G_{os}^* = 0$, one can obtain instead of Eq. (2)

$$k_f = k_0\exp(-\Delta G_{is}^*/RT), \tag{12}$$

where ΔG_{is}^* can be regarded as the activation energy of the reaction. In this case, preexponentional factor k_0 in expression (12) for the rate constant in the least viscous phase (k_f) is obviously independent of γ and τ_L. Then, the following expression can be obtained for the reaction rate constants in a real viscous medium from Eqs. (2), (3), (5), and (12)

$$k \sim k_f\tau_L^{-1}(\Delta G_{os}^*/RT)^{1/2}\exp(-\Delta G_{os}^*/RT) \sim k_f/\tau_c, \tag{13}$$

i.e., this model predicts the proportionality between the reaction rate constants in viscous and nonviscous liquids and cannot explain the reactivity-leveling effect for the case when dependences of the $k \sim k_f^m$ type were found experimentally for $m < 1$ (see Refs. 18—20).

The model of the indirect cage effect[21] qualitatively explains both the correlation between reaction kinetics and molecular mobility and the leveling effect. By analogy with this model, one can assume that an elementary chemical reaction in a polar medium with restricted molecular mobility proceeds *via* a metastable state which corresponds to the structure of an activated complex in a nonviscous medium (in a free volume) but is attained through overcoming the additional relaxation activation barrier E_r, the height of which is determined by an intersection point of the parabolic terms:[21]

$$E_r = (\Delta G_{os}^* + \Delta G_{is}^*)^2/4\Delta G_{os}^*. \qquad (14)$$

Generally, one can accept $\Delta G_{is}^* < \Delta G_{os}^*$ for rough estimates

$$E_r \approx \Delta G_{os}^*/4 + \Delta G_{is}^*/2. \qquad (15)$$

Then, the following expression should be written for the rate constant instead of Eq. (2)

$$k = k_0\exp(-\Delta G_{os}^*/4RT - \Delta G_{is}^*/2RT) \sim k_r^{1/2}k_0\exp(-\Delta G_{os}^*/4RT). \qquad (16)$$

It is clear that Eq. (6), which relates the rate constant to parameters γ and τ_L, is still valid, whereas Eq. (16) describes the reactivity-leveling effect.

Thus, using the example of metallotropy of the substituted 2-(stannyloxy)phenoxyl radical in solvents of various polarity, it is shown that the solvent-reorganization model, which takes into account the indirect cage effect, allows one to qualitatively interpret the available data on the rate constants of elementary reactions under conditions of restricted molecular mobility, *i.e.*, in viscous polar media.

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