LIGAND SUBSTITUTION REACTIONS IN NON-REGULAR CONDENSED SYSTEMS

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Abstract: *Some problems of ligand substitution reactions in non-regular condensed systems are considered in this work. One of the aspects of theoretical research is the study of the properties of individual particles, taking into account the nano-dimension of the molecules of the condensed system surrounding the particle. Two main mechanisms of influence on ligand particles from the medium, solvation and fluctuation, are distinguished. In numerical calculations of ligand substitution reactions, it is convenient to separate the reorganization of the reagent molecules and the reorganization of the medium during the process. Analytical expressions for the kinetic parameters of a wide class of reactions were obtained.*

Keywords: *ligand substitution, condensed systems, spatial and frequency dispersion, solvation, impurity particles, Green functions, electron-nonadiabatic charge transfer, electron-adiabatic process.*
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Introduction

The modern theory of kinetics of charge transfer processes in nonregular condensed systems allows us to obtain analytical expressions for kinetic parameters of a wide class of reactions. When describing specific processes [1-7], it is very important to choose a system model that will consider the nature of the chemical reaction, describe the specific properties of the reacting particles, and take into account the effects of spatial and frequency dispersion of the medium.

To describe a condensed medium, it is convenient to use the apparatus of Green's functions of medium polarization operators, which allows one to take into account the effects of frequency and spatial dispersion. When describing reacting particles, it is necessary to take into account the possibility of their polarized and solvated state. To describe intramolecular oscillations of reagents, as a rule, it is sufficient to use the harmonic approximation, which works effectively for high-frequency oscillations. To take into account possible effects of anharmonicity of intramolecular vibrations of reagents, it is sufficient to use the Morse potential [8]. In this case, the parameters of this potential can be determined both by spectroscopic measurements and by thermodynamic data on the dissociation energy of a given chemical bond. Stronger effects of anharmonicity can be observed for deformation vibrations of reagents. To describe such effects, it is convenient to use the modified Poeschl-Teller potential [9].

The interaction of reacting particles with the medium is represented as the sum of two interactions: the interaction of fluctuations in the polarization of the medium with the static (Coulomb and dipole) field of the reacting particles and the interaction of fluctuations in the polarization of the medium with intramolecular vibrations of the reacting particles.

Probability of an elementary act of an electron-nonadiabatic charge transfer process. To calculate the probability of an elementary act of the electron-nonadiabatic charge transfer process, we use the results of the multichannel collision theory, within which the Hamiltonian of the system H is represented as the sum of the initial H_i and final H_f states and the channel interaction, respectively, the initial V_i or final V_f channels:

$$H = H_i + V_i = H_f + V_f \tag{1}$$

In the first order of perturbation theory with respect to the channel interaction of the initial channel, the expression for the probability of the system transition from the initial state i to the final state f can be used

$$W_{fi} = \frac{2\pi}{\hbar}\sum_{n,n'} e^{\beta(F_i - E_{in})} \left|\langle \Psi_i | V_i | \Psi_f \rangle\right|^2 \delta\left(E_{in} - E_{fn'}\right)_i; \qquad \beta = \frac{1}{kT} \tag{2}$$

where E_{in} and Ψ_i are the eigenvalues and eigenfunctions of the Hamiltonian of the initial state H_i; n is the index of the oscillatory state of the system in the initial state; similarly, E_{fn}, Ψ_f and n' are for the final state. F_i is the free energy of the system in the initial state.

For a-particle reaction, from formula (2) one can obtain for the rate constant

$$K_a = V^{a-1} W_{fi} \frac{1}{ikT} e^{\beta F_{ia}} \int_{-i\infty}^{i\infty} d\theta Sp\left[e^{-\beta(1-\theta)H_i} V_i e^{-\beta\theta H_f} V_i^f\right] \tag{3}$$

In this formula, the trace is assumed by all coordinates except for the electron coordinates of the reacting particles, V is the volume of the system, F_{ia} is the free energy of the system (a-reagents and the medium) in the initial state, and H_f is the Hamiltonian of the system in the final state.

After simple transformations, we obtain for the rate constant a-partial reaction:

$$K_a = \frac{1}{ikTV} e^{\beta \mathcal{F}_i} \int_{-i\infty}^{i\infty} d\theta Sp\left[e^{-\beta(1-\theta)H_i} V_i e^{-\beta\theta H_f} V_i^f\right] \tag{4}$$

In the last formula, $\mathcal{F}_i$ is the free energy of the system, independent of the volume of the system:

$$\mathcal{F}_i = F_{ia} + akTlnV$$

Further calculations of the rate constant of the charge transfer process are possible for specific processes within specific models. In this case, from the general expression for the rate constant of the process, calculations of the trace should be carried out for specific coordinates of a particular process. It should be taken into account that the coordinates can describe both classical processes and quantum ones - depending on the frequencies of the corresponding processes.

For the substitution reaction of ligands in linear complexes, the following expressions can be used:

$$AB + C^- \rightarrow AC + B^- \tag{5}$$

Where $A = CH_3Hg$ and C_6H_5Hg, $B = OH$ - group, $C = Cl, Br, I$

In these processes, a reorganization of the reacting particles occurs, during which some chemical bonds are broken (the bond $Hg - OH$ is broken) and others are formed (the bond $Hg - C$).

The frequencies of the $R - Hg - B$ deformation vibrations (here R is a part of the A fragment except for the Hg atom) are of the order of 50–140 cm^{-1}, so these frequencies can be considered classical. The frequencies of the stretching vibrations of the mercury ion are in the range 170–330 cm^{-1}, the frequency of the stretching vibration of $Hg - B$ in CH_3HgB is 386 cm^{-1}, and the frequency of the stretching vibrations of the OH group in H_3HgOH is 511 cm^{-1} and in C_6H_5HgOH is 560 cm^{-1}. As a result, all the stretching vibrations of these particles can be considered classical.

In numerical calculations of ligand substitution reactions, it is convenient to separate the reorganization of the reagent molecules and the reorganization of the medium during the process. It should be noted that to calculate the reorganization energy of the medium (E_{rm}), it is necessary to know the exact distribution of charges on the particles - reagents, which we do not know. But if we vary the charges on individual atoms and the correlation lengths of different polarization modes, we can obtain an approximate value of the reorganization energy of the medium, which for the reactions under consideration is in the range of 84-170 kJ/mol.

From the numerical values of the valence and deformation vibrations of the reagents, it can be concluded that both in the initial state and in the final state, the potential energy curve describing the valence vibrations of the reagents is steeper than the potential energy curve describing the deformation vibrations. As a result, in the transition configuration, the leaving group will have a bond length equal to the equilibrium bond length in the initial state, and the entering group will have a bond length equal to the equilibrium bond length of the final state. As a result, the intramolecular reorganization of the system is reduced to the reorganization of the deformation degrees of freedom of the system.

In the harmonic approximation, to calculate the reorganization energy of deformation vibrations (E_{rd}), one can use the formula:

$$E_{rm} = \frac{1}{2} K_d \vartheta_0^2 \tag{6}$$

Where ϑ_0 is the angle of closest approach of the reactants, and K_d is the effective value of the deformation force constant:

$$K_d = \frac{2K_{Bd}K_{cd}}{K_{Bd} + K_{cd}} \tag{7}$$

Here K_{Bd} and K_{cd} are the values of the deformation constants of molecules AB and AC.

The calculated values of K_{Bd} and K_{cd} for the reaction with phenyl derivatives mercury turned out to be in the range of 200–250 kJ/mol, and for the reaction with methyl derivatives of mercury, 400–650 kJ/mol. Of real interest are the calculations for these reactions, not only in the harmonic approximation, but also in the approximation within the framework of the Pöschl-Teller model, in which, as the potential of deformation vibrations, the following expression is used:

$$u_{pot} = D th^2 \sqrt{\frac{K_d}{2D}} \tag{8}$$

where D is the dissociation energy, equal to approximately 250 kJ/mol for the systems under study. At the same time, the reorganization energies for the systems under study do not exceed 250 kJ/mol.

Probability of an elementary act of the electron-adiabatic process of charge transfer.

For particles of spherically symmetric shape, the motion of which as wholes can be described in the classical approximation, the rate constant of the adiabatic process of charge transfer can be represented as

$$K = 4\pi G e^{-H(\theta)} \int_0^\infty L^2(R_{AB}) e^{-U(R_{AB})/kT} R_{AB}^2 dR_{AB} \tag{9}$$

where

$$H(\theta) = E_{rm}F_\omega(\theta) + \beta\theta\Delta F + \sum_n 2E_{rn} \left[ch\frac{\beta\omega_{fn}\theta}{2}\omega_{fn} + ch\frac{\beta\omega_{in}(1-\theta)}{2}\omega_{fn} \right]^{-1}$$

$$F_\omega(\theta) = \frac{2}{\hbar}\int \frac{d\omega}{\omega^2} f(\omega) \left[sh\frac{\beta\omega(1-\theta)}{2} \cdot sh\frac{\beta\theta\omega}{2} / sh\frac{\beta\omega}{2} \right] \tag{10}$$

Here $f(\omega)$ is the Green's function of the frequency dependence of the medium polarization operators $g_m(\vec{r},\vec{r'},\omega)$ normalized to unity in the approximation

$$I_m g_m(\vec{r},\vec{r'},\omega) = \pi g_m(\vec{r},\vec{r'},\omega = 0) f(\omega); \quad \int_{-\infty}^{\infty} \frac{f(\omega)}{\omega} = 1 \tag{11}$$

In formula (9) G has the form:

$$G = \sqrt{\frac{2\pi}{H''_{\theta\theta}}}\beta \prod_n exp\left[\frac{2\theta^*}{kT}(\omega_{fn} + \omega_{in})\right] sh\frac{\beta\omega_{in}}{2}\left\{sh^2\left[\beta\frac{\omega_{in}}{2}(1-\theta^*) + \frac{\beta\omega_{fn}}{2}\theta^*\right] + \frac{(\omega_{fn}+\omega_{in})^2}{4\omega_{fn}\omega_{in}} sh\big(\beta\omega_{in}(1-\theta^*)\big) sh\beta\omega_{fn}\theta^*\right\}^{-1/2} \tag{12}$$

In formula (10), ΔF is the difference in the slopes of the potential energy terms of the system in the initial and final states near their intersection point; ω_{in} and ω_{fn} are the frequencies of intramolecular vibrations of the reactants at the beginning (ω_{in}) and at the end (ω_{fn}) of the charge transfer process.

As the interaction potential $U(R_{AB})$, we will take an infinitely high wall at distances smaller than the sum of the particle radii and the Coulomb function at large distances.

Integrating in formula (9) using the saddle point method, we obtain

$$K = 4\pi G e^{-H(\theta^*)}(R^*_{AB})^2\delta \cdot L^2(R^*_{AB})e^{-U(R^*_{AB})/kT} \tag{13}$$

At a condition

$$|U'(R^*_{AB})| \cdot \frac{\delta}{2kT} \ll 1 \tag{14}$$

Here δ is the characteristic size of the decrease of the electron resonance integral.

When studying processes, it is possible not to calculate the electron resonance integral and to vary its value within certain limits, which will allow calculating the values of the kinetic parameters of the charge transfer process for both the non-adiabatic mechanism and the adiabatic mechanism for the electron. In this case, the critical value of the electron resonance integral L_c in the harmonic approximation for deformation vibrations has the form

$$L_c = \left[\frac{1}{2\pi^3}\left(2kT\omega_m^2 E_{rm} + kT\omega_{\omega d}/(K_{Bd}\alpha^2)\right)\right]^{1/4} \tag{15}$$

where ω_m is the characteristic frequency of oscillations of the medium molecules, E_{rm} is the reorganization energy of the medium, $\omega_{\omega d}$ is the characteristic frequency of oscillations of the reagent, $\alpha = \lambda_s - \lambda_{i,}$ λ_s and $\lambda_{i,}$ are the values of λ in the transition configuration (λ_s) and at the beginning of the process (λ_i).

If the process is adiabatic, then for the potential energy of the system the following expression can be used:

$$U(\lambda) = (\lambda_0 - \lambda + \lambda^2)E_{rm} + \frac{1}{2}[u_{Bd}(\lambda) + u_{cd}(\lambda)] - \frac{1}{2}\{[u_{Bd}(\lambda) - u_{cd}(\lambda) - \Delta F - (1-2\lambda)E^2_{rm}] + 4L^2\}^{1/2} \tag{16}$$

Where λ_0 has the form

$$\lambda_0 = \frac{1}{2} + \frac{\Delta F}{2E_{rm}} \tag{17}$$

For the harmonic approximation, the function $U(\lambda)$ takes the form

$$U(\lambda) = \frac{1}{2}\left\{\Delta F + (1 - 2\,\lambda + 2\lambda^2)E_{rm} - \frac{1}{2}[\Delta F + (1 - 2\,\lambda)E_r]^2 - 4L^2\right\}^{1/2} \tag{18}$$

where E_r is the total reorganization energy of system:

$$E_r = E_{rm} + E_{rd} \tag{19}$$

As studies of the function $U(\lambda)$ in formula (18) show, it has two minima and one maximum when two conditions are met simultaneously:

$$\frac{2L}{E_r} < 1; \ \left[1 - \left(\frac{2L}{E_r}\right)^{2/3}\right]^{3/2} > \frac{\Delta F}{E_r}\ ; \tag{20}$$

With an increase in the parameter L or ΔF, the $U(\lambda)$ curve has only one maximum, and formally the activation energy for the forward reaction (at $\Delta F < 0$) or for the reverse reaction ($\Delta F > 0$) will turn to zero.

The equation for calculating θ^* in the harmonic approximation is

$$\Delta F + (1 - 2\,\theta)E_{rm} = \frac{E_{rB}\left[\theta^2 - \text{æ}(1-\theta)\right]^2}{[\theta + (1-\theta)\text{æ}]^2} \tag{21}$$

And in the case of equal frequencies at the beginning and end of the transfer process, the last equation is solved exactly

$$\theta^* = \frac{1}{2} + \frac{\Delta F}{2E_r} \tag{22}$$

For adiabatic processes, the equation for determining θ^* in the harmonic approximation has the form

$$\frac{E_{rB}}{\frac{\text{ǽ}}{\theta} + (1-\text{ǽ})^2} - \frac{\text{ǽ}E_{rB}(1-\theta)^2}{[\text{ǽ} + (1-\text{ǽ})\theta]^2} + 2E_{rm}\left(\theta - \frac{1}{2} - \frac{\Delta F}{2E_{rm}}\right) + \frac{L(1-2\theta)}{\sqrt{\theta(1-\theta)}} = 0 \tag{23}$$

Here ǽ is the transmission coefficient

$$\text{ǽ} = (1 - e^{-\gamma_e})/(1 - 0.5e^{-\gamma_e}) \tag{24}$$

Where γ_e is the parameter

$$\gamma_e = 2\pi L^2/(|v||\Delta F|) \tag{25}$$

In the relation (25), v is the speed of the system near the transition configuration of the system.

The solution of the last equation leads to three values of θ^*, which correspond to the minima of the initial and final states and the transition configuration.

The activation energy of a nonadiabatic process can be determined for the harmonic approximation:

$$E_a = (\theta^*)^2 E_{rm} + \frac{K_{Bd}}{2}\vartheta_0^2\left(1 + \frac{1-\theta^*}{\theta^*}\,\text{ǽ}\right)^{-2} \tag{26}$$

and for a potential of type u_{p_0t} the activation energy of the process has the form

$$E_a = \left[\frac{D_c}{2E_{rm}} \cdot \frac{(t_0 - t_\alpha)^2}{(t_0 + t_\alpha)^2} - \frac{D_B}{2E_{rm}} \cdot \frac{(1-t)^2}{(1+t)^2} + \frac{E_{rm} + \Delta F}{2E_{rm}}\right]^2 \cdot E_{rm} + D_B \left(\frac{1-t}{1+t}\right)^2 ; \quad (27)$$

$$t_0 = exp\left[\sqrt{\frac{2K_{Bd}}{D}}\,\vartheta_0\right]; \qquad t = exp\left[\sqrt{\frac{2K_{Bd}}{D}}\,\vartheta_B^*\right]$$

For adiabatic processes it is necessary to calculate the transition configuration of the transfer process for a specific process, and the activation energy will be equal to the difference in potential energies at the point of maximum potential energy of the process and at the initial point. Due to the cumbersomeness of theoretical calculations, the results for adiabatic ligand substitution reactions obtained in numerical calculations are given below in Tables 1-4.

The partial contribution of the medium E_{am} to the total activation E_a energy can be determined only for nonadiabatic processes and is equal to

$$E_{am} = (\theta^{*2})\, E_{rm} \quad (28)$$

Tables 1–3 present the results of calculations of the parameters of the ligand substitution transfer process using the harmonic approximation for the deformation vibrations of reagents, and Table 4 for the modified Poeschl-Teller potential (MPTP). The parameters E_{rm} and L were selected individually.

Table 1. Kinetic parameters of nonadiabatic ligand substitution reactions. Harmonic approximation for deformation vibrations. *Erm*, *Ea* - in kJ/mol; $K_{Bd} = K_{Cd}$.

R	X^-	Erm	θ^*	E_a
C_6H_5	Cl	84	0.54	84.9
	Br	167	0.53	105.8
	I	84	0.53	87.8
	Cl	167	0.52	108.7
	Br	84	0.51	90.7
	I	167	0.50	111.2
CH_3	Cl	84	0.53	134.6
	Br	167	0.52	156.8
	I	84	0.51	162.6
	Cl	167	0.51	183.5
	Br	84	0.50	194.4
	I	167	0.51	214.9

Table 2. Kinetic parameters of adiabatic ligand substitution reactions. Harmonic approximation for deformation vibrations. *Erm, Ea, L* - in kJ/mol.

R	X^-								
		E_{rm}	L	α	E_a	E_{rm}	L	α	E_a
C_6H_5	Cl	84	42	0.49	47.7	167	84	0.46	36.4
	Br	84	42	0.44	50.2	125	84	0.41	29.7
	I	84	42	0.41	55.2	84	84	0.34	24.7
CH_3	Cl	84	167	0.33	14.2	167	188	0.35	19.2
	Br	84	167	0.27	34.7	125	188	0.26	30.1
	I	84	167	0.21	85.3	84	188	0.20	71.5

Table 3. Kinetic parameters of adiabatic ligand substitution reactions. Harmonic approximation for deformation vibrations. *Erm, Ea, L* - in kJ/mol.

R	X^-	$K_d = \frac{2K_{Bd}K_{cd}}{K_{Bd} + K_{cd}}$	$K_d = \frac{2K_{Bd}K_{cd}}{K_{Bd} + K_{cd}}$

		E_{rm}	L	α	E_a	E_{rm}	L	α	E_a
C_6H_5	Cl	167	84	0.46	36.4	167	31	0.55	39.3
	Br	125	84	0.41	29.7	125	31	0.51	27.6
	I	84	84	0.34	24.7	84	31	0.42	14.2
CH_3	Cl	167	146	0.41	40.5	167	42	0.51	43.1
	Br	125	220	0.20	14.2	125	52	0.41	28.4
	I	84	272	0.13	24.7	84	63	0.23	18.8

Table 4. Kinetic parameters of adiabatic ligand substitution reactions. The MPTP potential was used for deformation vibrations. $E_{rm}, E_a, L,\ \Delta F -$ are measured in - kJ/mol.; $\vartheta_{0,}\ \vartheta_B^*$ in - rad.; K in – l/mol. Sec.

R	X^-	E_{rm}	L	$\vartheta_{0,}$	$K_{Bd} = K_{Cd}$			lgK	ΔF
					ϑ_B^*	α	E_a		
C_6H_5	Cl	167	84	1.24	0.716	0.48	36.8	4.99	44.3
	Br	125	84	1.28	0.709	0.43	30.5	6.02	38.5
	I	84	84	1.t35	0.697	0.41	24.2	6.90	33.9
CH_3	Cl	167	146	1.24	0.677	0.39	40.5	4.33	48.1
	Br	125	220	1.28	0.672	0.29	30.5	5.65	40.5
	I	84	272	1.35	0.683	0.18	32.6	2.94	56.0

Conclusion

In the framework of theoretical models of the kinetics of charge transfer processes in nonregular condensed systems, analytical expressions for the kinetic parameters of a wide class of reactions were obtained. It was shown that in describing specific processes, it is very important to choose a model of the system within which it is possible to take into account, in a certain model approximation, the nature of the chemical reaction and describe the specific properties of the reacting particles. Under certain conditions, it is possible to take into account the effects of spatial and frequency dispersion of the medium. The interaction of reacting particles with the medium can be represented as the sum of two interactions: the interaction of the polarization fluctuations of the medium with the static (Coulomb and dipole) field of the reacting particles and the interaction of the polarization fluctuations of the medium with the intramolecular oscillations of the reacting particles. Specific theoretical models of the process are selected, and the corresponding parameters are calculated. In this case, for the deformation vibrations of the reagents, the effects of anharmonicity are taken into account for some calculations, and, in particular, the Poeschl-Teller potential is used.

References

1. Tai H.-Ch., Lim C. Computational Studies of the Coordination Stereochemistry, Bonding, and Metal Selectivity of Mercury. *The Journal of Physical Chemistry A*, 2006, **Vol. 110(2)**, p. 452-62. DOI: 10.1021/jp0529826.
2. Van Damme S., Dufrêch J.-F., Deconinck J. Influence of Ion Properties on the Equilibrium and Transport Properties of Electrolyte Solutions. *The Journal of Physical Chemistry B*, 2006, **Vol. 110(2)**, p. 1015-1019.
3. Seelen E., Liem-Nguyen V., Urban W., Baumann Z., Mason R., Skyllberg U., Björn E. Dissolved organic matter thiol concentrations determine methylmercury bioavailability across the terrestrial-marine aquatic continuum. *Nature Communications*, 2023, **Vol. 14**, Article number: 6728, 13 p.
4. Jordan R.B. *Ligand Substitution Reactions***.** *In book: Reaction Mechanisms of Inorganic and Organometallic Systems*. 2007. p. 43–113, DOI: 10.1093/oso/9780195301007.003.0005, July 2007.
5. Wilkins R.G. *Kinetics and Mechanism of Reactions of Transitional Metal Complexes*.

2002. WiJey- VCH Verlag GmbH & Co. KGaA. 311 p.

6. Bruice P.Y. *Organic Chemistry (6th ed.*). 2011.1900 E. Lake Ave., Glenview. IL 60025: Pearson Education Inc. p. 332–365. ISBN 978-0-321-66313-9.
7. Tao G., Stratt R.M. Why Does the Intermolecular Dynamics of Liquid Biphenyl so Closely Resemble that of Liquid Benzene? Molecular Dynamics Simulation of the Optical-Kerr-Effect Spectra. *The Journal of Physical Chemistry B.*, 2006, **Vol. 110(2)**, p. 976-987.
8. Flügge S. *Practical Quantum Mechanics*. 1971. Vol. I, II. Springer. Berlin.
9. Pöschl G., Teller E. Bemerkungen zur Quantenmechanik des anharmonischen Oszillators. *Zeitschrift für Physik*, 1933, **Vol. 83**, p. 143-151. DOI:10.1007/BF01331132.