



Title	THE THEORY OF THE KINETICS OF THE LIGAND SUBSTITUTION PROCESSES IN THE COORDINATION SPHERE OF THE METAL COMPLEXES
Author(s)	GERMAN, E. D.; DOGONADZE, R. R.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 20(1), 34-49
Issue Date	1972-04
Doc URL	http://hdl.handle.net/2115/24934
Type	bulletin (article)
File Information	20(1)_P34-49.pdf



[Instructions for use](#)

THE THEORY OF THE KINETICS OF THE LIGAND SUBSTITUTION PROCESSES IN THE COORDINATION SPHERE OF THE METAL COMPLEXES

By

E. D. GERMAN*) and R. R. DOGONADZE*)

(Received December 26, 1971)

Abstract

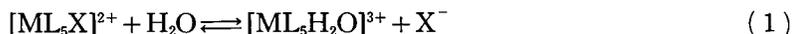
The ligand substitution processes in the coordination sphere of the octahedral metal complexes [of Cr(III), Co(III) and Rh(III)] is analyzed on the basis of previously developed quantum mechanical theory of chemical reactions. The expression obtained for the energy of activation contains three parameters. One of this is estimated theoretically, two the others from a comparison of the theory with experimental data for the aquation reactions of $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ complexes. The values obtained for the kinetic parameters have been applied in the calculation of energies of activation for some other ligand substitution reactions.

Introduction

The ligand substitution reactions in the coordination sphere of the metal complexes are often intermediate stages in the catalysis by metal complexes^{1,37)} so that the investigation of such processes is of considerable interest.

The modern concepts about the mechanism of the substitution reactions in the complexes are based primarily on the experimental studies.

In the present paper the theoretical investigation of these reactions is presented. As a model processes the aquation reactions of octahedral metal complexes of Cr(III) and Co(III)



where $\text{L} = \text{H}_2\text{O}, \text{NH}_3$; $\text{X}^- = \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NCS}^-, \text{NO}_3^-, \text{N}_3^-$ are considered.

Such processes also involve a charge transfer from the complex $[\text{ML}_5\text{X}]^{2+}$ to the ligand X^- , resulting in the formation of a new ion $[\text{ML}_5\text{H}_2\text{O}]^{3+}$, of charge $3|e|$, and a free ion X^- .

A quantum-mechanical theory of the kinetics of reactions involving

*) Institute of Electrochemistry, Academy of Sciences of USSR, Moscow, USSR.

The Theory of the Kinetics of the Ligand Substitution Processes

charge transfer or redistribution in polar media was developed in a series of papers^{2,3}, the basic conclusions of which can be summarized as follows.

All degrees of freedom, which characterize the reacting particles and solvent, can be divided into classical and quantum degrees of freedom. The general basis of the division is given in reference⁴, but qualitatively the criteria for a quantum (classical) degree of freedom can be formulated in the following way: if the energy of the characteristic frequency ($\hbar\omega_{cl}$) of a given degree of freedom is smaller than $4kT$, then the motion along this degree of freedom is classical, *i.e.* it goes over the potential barrier. Motion along a degree of freedom, the characteristic vibration energy ($\hbar\omega_{qu}$) of which is higher than $4kT$ is a quantum motion, *i.e.* of subbarrier nature.

A dynamical model^{*)} for the solvent is applied in the quantum theory. The physical idea of this model can be illustrated by redox reactions in which an electron is transferred from an ion A^{z_1} to an ion B^{z_2} .

When a redox reaction takes place in the gas phase, then according to the energy conservation law, the electron energy change must be compensated by a change of the kinetic energy of the particles A^{z_1+1} and B^{z_2-1} , *i.e.* by a change of their velocities. The velocities of the heavy particles must change practically instantaneously, as the characteristic time of the electron jump from one ion to another is of the order of 10^{-15} sec. This leads to a very small electron transfer probability for large values of $(\mathcal{E}_A - \mathcal{E}_B)$. Experiments show that the transition probability is in fact different from zero only if \mathcal{E}_A is approximately equal to \mathcal{E}_B . This experimental fact is known as the Frank-Condon principle. Considering the same reaction in a polar liquid one must take into account, that the electron energy levels of the ions A^{z_1} and B^{z_2} depend not only on the interaction of the electron with the ion cores, as in the gas phase, but also on the interaction of the electron with the polarized medium, *i.e.* with the dipoles of the solvent. This change of electron energy in going from the gas phase to a polar liquid is comparable with the electrostatic part of the solvation energy of the ions and can amount to several dozens of kcal/mole. It is important for

*) Within this theory the solvent is considered in a way which differs essentially from the approach of the theory of absolute rates. In the latter theory the influence of the solvent is accounted for by including in the activation energy, the difference of the solvation energies of transition and initial states. The energies of these states are calculated by means of the Born formula or some improved formula of this kind. When calculating the solvation energy of the initial and final states, it is usually assumed that the medium polarization is in equilibrium with the electrostatic field. Therefore, according to the theory of absolute rates, the whole influence of the solvent upon the kinetics can be described by means of one single parameter — the static dielectric permeability of the medium.

E. D. GERMAN and R. R. DOGONADZE

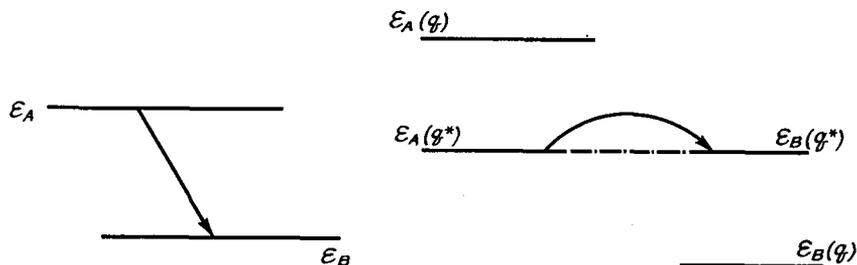


Fig. 1.

the electron transfer kinetics that the thermal motion of the solvent dipoles, *i. e.* the polarization fluctuations, changes the interaction energy of the electron with the polarization of the medium. Thus, the electron energy levels essentially depend on the dipole configuration in every moment, as opposed to the gas phase reactions. This dependence is shown schematically in Fig. 1. Here q is some set of normal coordinates, describing the time-dependent configuration of the dipoles, *i. e.* the fluctuating polarization of the medium. It can be seen easily, that according to the Frank-Condon principle, the electron transfer can take place only if \mathcal{E}_A , as a consequence of the polarization fluctuation of the medium, becomes approximately equal to \mathcal{E}_B . In the situation where the coordinate q is equal to q^* , the electron energy change during the transition is practically equal to zero, and the velocities of the heavy particles, *i. e.* of the ions and dipoles of the medium, do not necessarily change instantaneously, *i. e.* during 10^{-15} sec, here, in the transition state, *i. e.* activated complex, the solvent dipoles have a definite configuration q^* .

Thus the *dynamical* properties of the medium, *i. e.* the characteristic frequencies ω and the intensity of the polarization fluctuations—which can be found from the dependence of the dielectric permeability on the frequencies—are important in the theory. For water the most intensive absorption takes place in the frequency range $1-10\text{ cm}^{-1}$, which is considerably smaller than $4kT$. This classifies, according to the criteria given above, the vibration frequencies along the coordinates q as classical.

Thus, in electron transfer reactions the electron, as the only quantum subsystem, undertakes a subbarrier motion while the movement along the solvent coordinate is classical and passes over the barrier.

The principles mentioned may be summarized to explain the mechanism of the elementary act of arbitrary chemical reactions involving a charge transfer or a charge redistribution. In the transition state of an arbitrary chemical reaction, levelling of the energy levels must take place for each degree of freedom along which quantum motions occur. This may be effec-

The Theory of the Kinetics of the Ligand Substitution Processes

tuated by means of fluctuation of the solvent polarization and fluctuational deformation of the intra-molecular degrees of freedom, along which the classical overbarrier motions occur. Consequently, the activation energy will be determined exclusively by the classical subsystem.

Analysis of Experimental Data

We now consider substitution processes within the quantum-mechanical theory of chemical reaction¹⁻³. At present the question of the mechanism of aquation reactions of octahedral complexes is not settled definitely. Thus, in general distinction between S_N1 and S_N2 mechanisms can not be given unambiguously. Below we shall analyze reaction (1) assuming a bimolecular substitution mechanism. We shall consider a model, in which no formation of a kinetically independent seven-coordinate intermediate occurs. Obviously, other mechanism must be taken into account. For example the H_2O molecule may move to a position between X^- and a neighboring water molecule in the complex. This mechanism as well as the S_N1 mechanism will be considered in later communication.

In general the stretching frequencies of the $M-X$ bond in complexes $[ML_5X]^{2+}$ do not exceed 700 cm^{-1} .⁵ The vibration frequencies of the free ions X^- in the solvent are much smaller the order of magnitude being roughly the same as the reverse Debye relaxation time. On the other hand, the vibration frequency along the degree of freedom, describing the motion of the H_2O molecule, undergoes an abrupt increase during the reaction, as

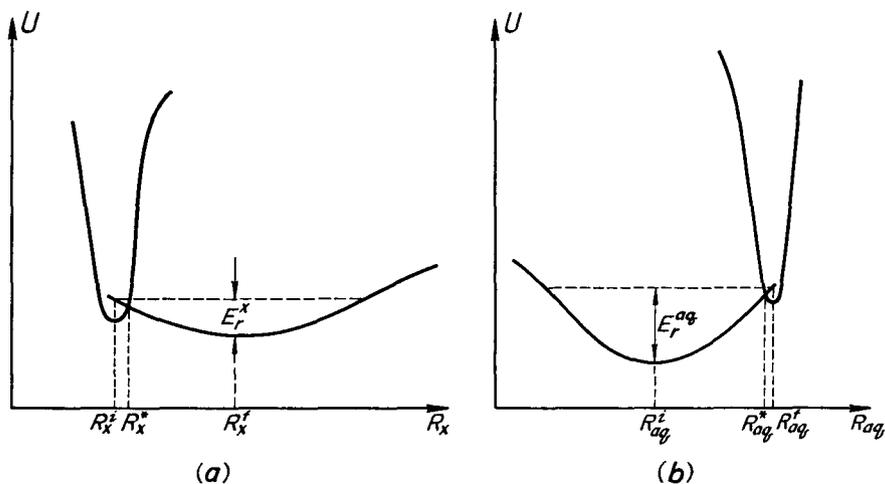


Fig. 2.

the water passes from the solvent into the complex, where the characteristic M-OH₂ bond stretching frequencies lay in the range 400–650 cm⁻¹. This is illustrated in Fig. 2 a and b, where the terms of the initial and final states are shown. The chemical bond M-X in the activated state is practically not stretched ($R_x^* \approx R_x^f$) and the coordinate of H₂O almost coincides with the equilibrium coordinate in the final state ($R_{aq}^* \approx R_{aq}^f$). The activated state along the coordinate of the solvent is shown in Fig. 3. These figures also define the parameters, which are important in the theory, *i.e.* the reorganization energies corresponding to the various degrees of freedom in the initial and the final equilibrium state (E_r^x , E_r^{aq} and E_s) (A more detailed description of E_s can be found in ref. 2). The expression for the activation energy, of the assumed reaction mechanism (1) has the form

$$E_a = E_r^{aq} + \frac{[E_s + \Delta I + E_r^x - E_r^{aq}]^2}{4E_s} \quad (2)$$

where ΔI is the distance between the minima of the potential energy surfaces of the initial and final state. For the reactions considered it practically coincides with heat of reaction (ΔH_0).

According to equation (2) the Brønsted coefficient α determined by $\alpha = dE_a/d(\Delta I)$, has the form

$$\alpha = 1/2 + \frac{\Delta I + E_r^x - E_r^{aq}}{2E_s} \quad (2a)$$

and depends not only on the relative positions of the terms of the initial and final states (that is from ΔI), but also on the values of the three reorganization energies.

The kinetic parameter E_s contained in the formula (1), can be calculated theoretically⁶⁾, when the configuration of the reacting particles in the initial and final states, as well as their charge distributions are known. To estimate theoretically the parameters E_r^x and E_r^{aq} one has to know the particular kind of potentials which determine the movement of the particles X⁻ and H₂O in the proximity of the complex. It should be noted that the form of the

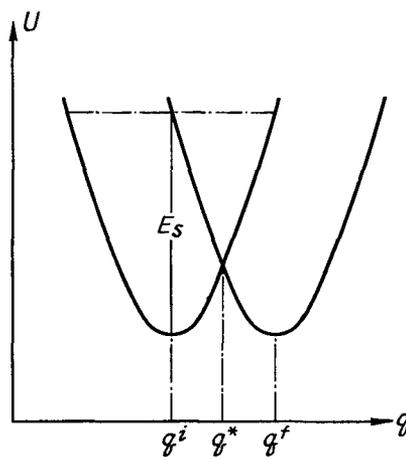


Fig. 3.

The Theory of the Kinetics of the Ligand Substitution Processes

potential curves depends on the direction in which the H₂O molecule attacks the position occupied by the ion X⁻ in the complex, and also on the direction along which X⁻ leaves the complex. This form can only be found by means of quantum-mechanical calculations. In the present work we estimated E_r^x and E_r^{aa} from two experimental points of known E_a and ΔI assuming that (2) contains values of the quantities E_r^x and E_r^{aa} corresponding to the most probable directions of the motion and orientation of the reagents and products, and assuming that they only undergo an insignificant change throughout the series of reactions considered.

To calculate the parameter E_s we shall represent the original complex $[ML_5X]^{2+}$ and the final complex $[ML_5H_2O]^{3+}$ as spheres of radius a . According to X-ray data⁷⁾, the value of a is about 3 Å. The radii of the ions X⁻ in the solutions will be assumed to be equal to their crystallographic radii. Also, in estimating E_s we shall neglect any asymmetry of the charge distribution in $[ML_5X]^{2+}$, assuming that the magnitude of the effective charge on X is small. Thus, the initial state is represented by a sphere of radius a on which the charge $(+2|e|)$ is uniformly distributed. The final state is represented by one sphere of charge $(3|e|)$ and one sphere of charge $(-|e|)$ at a distance r from the first sphere (fig. 4). Using this model the expression for E_s takes a form analogous to the one obtained by Marcus⁸⁾ for electron transfer reactions

$$E_s = C \cdot (1/2a + 1/2b - 1/r) \quad (3)$$

where C is a constant, which for reactions in water, equals $186 \text{ (kcal/mol)} \cdot \text{Å}$, when a , b , and r are expressed in Å. The distance r was chosen in such a way ($r \approx 5 \text{ Å}$) that the average value of E_s for three different X⁻ (e.g. X⁻ = Cl⁻, Br⁻ and I⁻) corresponded to the average value of E_s determined by equation (2) from three experimental points of the same X⁻, neglecting any variation of the parameters E_s , E_r^x and E_r^{aa} . The values of E_a and $\Delta I (\equiv \Delta H_0)$ used in estimating the average value of E_s are given in Table 1. The values of E_s calculated from equation (3) for X⁻ = Cl⁻, Br⁻ and I⁻ varied from 47 to 40 kcal/mol, while the value for the fluoride ion was found to be higher (65 kcal/mol).

Estimates of E_r^x and E_r^{aa} were also made

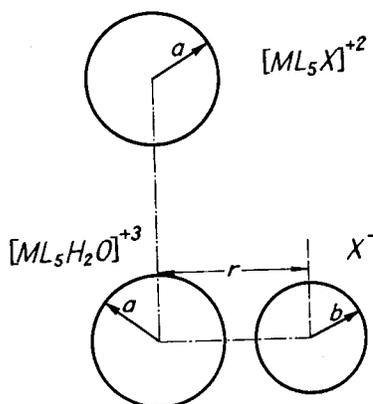


Fig. 4.

E. D. GERMAN and R. R. DOGONADZE

TABLE 1. Experimental values*) of the kinetic and thermodynamic parameters of the aquation reaction $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+} + \text{H}_2\text{O} \xrightleftharpoons{k_1} [\text{Cr}(\text{H}_2\text{O})_6]^{3+} + \text{X}^-$

X	$\log k_1^{\text{a)}}$	$-\log K_X^{\text{b)}}$	$\Delta H^{\text{c)}}$ kcal/mole	$\Delta S^{\text{d)}}$ e.u.	ΔH_0 kcal/mole	$\Delta S_0^{\text{e)}}$ e.u.	Ref.	
F	-9.2		28.7 ± 0.6	-3.9 ± 1.8			9	
		-4.33				-3.9	-20.2	10
Cl	-6.6		24.3 ± 0.2	-7.1 ± 0.5			9, 10	
		0.96				-6.0 ± 0.7	-7.7 ± 2	10, 11
						-6.6 ± 0.5		12
Br	-5.2		23.8 ± 0.3	-3.5 ± 0.9			10, 13	
		2.65				-5.1	-3.1	10, 14
I	-4.1		23.0 ± 0.3	-0.2 ± 0.9			9	
		5.0				-7.6	1.4	10
				28.0	16.4			15
NO ₃	-4.1		21.6 ± 0.1	-5.1 ± 0.2			16	
		2.0		21.4 ± 0.2	-5.7 ± 0.6	-4.5 ± 0.2	2.1 ± 0.6	17
NCS	-8.0	-3.1	27.5	1.9	2.1	1.1	18	
		-2.3						10
N ₃	-7.2		32.4	16.2			19	

*) at 25°C in aqueous solution.

a) $k_1 \text{ sec}^{-1}$; b) $K_X = \frac{[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}}{[\text{X}^-] \cdot [\text{Cr}(\text{H}_2\text{O})_6]^{3+}}$; c) $E_a = \Delta H^\ddagger + RT$;
d) evaluated using the frequency factor $\nu = 10^{13} \text{ sec}^{-1}$; e) $\Delta S_0 = \Delta S_{0X} + 8$, ΔS_{0X} being the experimental entropy $\Delta S_{0X} = 2.3 RT(\log K_X + \Delta H_0/kT)$

using data for substitution reactions in complexes of Cr(III) (Table 1). For E_r^x and E_r^{aq} the values ~ 5 kcal/mole and ~ 21 kcal/mole respectively, were obtained. It should be noted that the reorganization energy of the water molecule E_r^{aq} for reactions in aqueous solution is independent of X^- and M. As follows from equation (2) E_r^{aq} is the minimum activation energy for such reactions. In fact, when comparing with the experimental data given in Tables 2-4, one can see that activation energies smaller than 21 kcal/mole are practically not observed. Therefore we can conclude that E_r^{aq} contributes to a large extent to the total activation energy of aquation reactions of octahedral complexes, and this accounts for the rather small variation of experimental values of activation energies.

The Theory of the Kinetics of the Ligand Substitution Processes

TABLE 2. Experimental values*) of the kinetic and thermodynamic parameters of the aquation reaction $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \xrightleftharpoons{k_1} [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-$

X	$\log k_1$	$-\log K_X$	ΔH^\ddagger kcal/mole	ΔS^\ddagger e.u.	ΔH_0 kcal/mole	ΔS_0 e.u.	Ref.
F	-6.6		24.4	- 8.0			20
	-7.0		26.0	- 2.8			21
Cl	-5.14		22.9	- 5.4			22
	-5.06		22.3	- 6.9			23
	-5.0		21.8	- 8.2			24
	-4.6	~0	20.7 ± 1.1	-10.0	-6.0	-11	25
	-5.0		22.2	- 6.2	-1.8	5	26
Br	-4.0		20.9	- 5.5			24
I	-3.0		20.8	- 1.4			24
NCS	-7.0		24.7	- 6.9			27
	-7.1		24.9	- 7.8			28
	-6.4	~-1.85	29.6	11.0	6.0	- 2	25
NO_3	-3.1		21.0	- 3.0			29

*) at 25°C in aqueous solution; see footnotes. a)-e) of Table 1.

In order to calculate the activation energy series of analogous processes, use will be made of kinetic parameters of $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ complexes for all the series considered. Estimates of the energies of activation can be made in cases where the heats of the actual reactions are known. Results of the calculations, together with the average experimental values are given in Table 5. Taking into account the approximations made, the agreement can be considered satisfactory. This gives some support to the assumption that the reactions considered above really take place by an S_N2 mechanism. A definite answer to this question can only be given after a theoretical analysis of other mechanisms.

It should be noted that for constant values of the kinetic parameters E_s , E_r^{aq} and E_r^X , equation (2) expresses a correlations between activation energies and reaction heats $\Delta I (\equiv \Delta H_0)$. Thus, if the change in entropy of reaction and the entropy of activation throughout a series of reactions is not too drastic, equation (2) gives the relation (strictly speaking, non-linear) between the logarithm of the rate constant ($\log k$) and the logarithm of the

E. D. GERMAN and R. R. DOGONADZE

TABLE 3. Experimental values*) of the kinetic and thermodynamic parameters of the aquation reaction $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \xrightleftharpoons{k_1} [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-$

X	$\log k_1$	$-\log K_x$	ΔH^\ddagger kcal/mole	ΔS^\ddagger e.u.	ΔH_0 kcal/mole	ΔS_0 e.u.	Ref.
F	-7.1		20.7	-23.3			21, 30
	-5.2						31
	-5.8	-4.0	23.3	-6.9	-2.4	-18.2	30, 32, 33
Cl	-5.8		23.7	-6.0			34
		-0.15			-3.4	-4.0	35
		-0.18			-0.4	-1.6	23
		-0.10					36, 37
Br	-5.2		23.2	-2.7			30, 32
		0.43	24.0	-4.0			36, 37
I	-5.0		19	-27.6			21
NO ₃	-4.6	1.1	25.4	6.4			30, 36, 37
			24.3	1.9			38
NCS	-9.5	-2.67	30.1	~0			27, 36, 37
	-8.6		26.8	-8.4			28
N ₃	-8.7		33.1 ± 1.0	14			32
		-2.9		13.5		~0	39

*) at 25°C in aqueous solution; see footnotes. a)-e), Table 1.

corresponding equilibrium constant ($\log K$). Here it must be emphasized that the existence of a correlation between the $\log k$ and $\log K$ (Fig. 5), or between the activation energy and the reaction heat (Fig. 6) is *not* a criterion of a given mechanism, and therefore *it can not* be used to distinguish, *e.g.* between an S_N1 and S_N2 mechanism, as it was done for example in a book by LANGFORD and GRAY⁴²⁾.

If a relation between the rate constants and the corresponding equilibrium constants is established, then significant changes in ΔS^\ddagger and ΔS_0 may lead to an erroneous inclusion in the series, of reactions having other values of the kinetic parameters E_a , E_r^x or E_r^{aq} , *i.e.* to a violation of the assumption that ΔH_0 is the only parameter changing throughout the series. Thus, from the plots of E_a against ΔH_0 for the aquation reactions of Cr(III) complexes (Fig. 6)

The Theory of the Kinetics of the Ligand Substitution Processes

TABLE 4. Experimental values*) of the kinetic and thermodynamic parameters of the aquation reaction $[\text{Rh}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \xrightleftharpoons{k_1} [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-$

X	$\log k_1$	$-\log K_x$	ΔH^\ddagger kcal/mole	ΔS^\ddagger e.u.	ΔH_0 kcal/mole	ΔS_0 e.u.	Ref.
Cl	-6.4	-2.9	23.8	- 7.1	-3.8	-1.84	33
			22.2	-14.1			40
Br	-7.2		24.4	- 8.7			40
			24.6		-0.7 ± 0.4		41
I	-7.7		26.7	- 3.2			40
			26.2 ± 0.2		1.9 ± 0.3		41

*) at 25°C in aqueous solution; see footnotes. a)-e), Table 1.

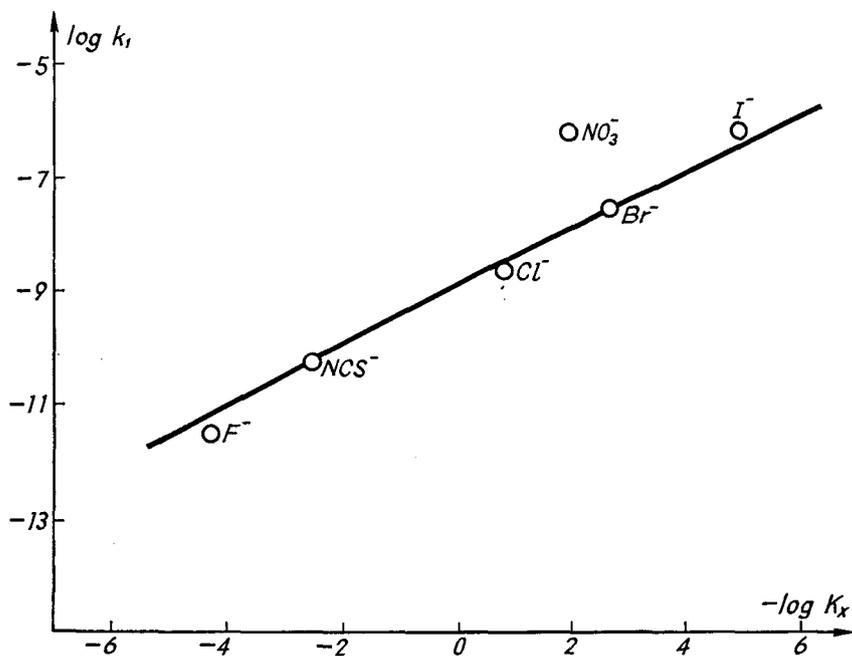


Fig. 5.

E. D. GERMAN and R. R. DOGONADZE

TABLE 5. Comparison of Experimental*) and Calculated Energies of Activation

Reaction	E_a^{calc} kcal/mole	ΔH_0 kcal/mole	$E_a^{\text{exp.}}$ kcal/mole
$[\text{Co}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-$			
X = Cl	24.8	-2.9	24.1
N ₃	28	6.5	33.1
$[\text{Rh}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Rh}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-$			
X = Cl	25.0	-2.6	24.6
Br	25.5	-0.7	25.1
I	26.3	1.9	27.1
$[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{3+} + \text{X}^-$			
X = Cl	24.5	-3.9	22.6
NCS	27.8	6.9	26.7

*) at 25°C in aqueous solution

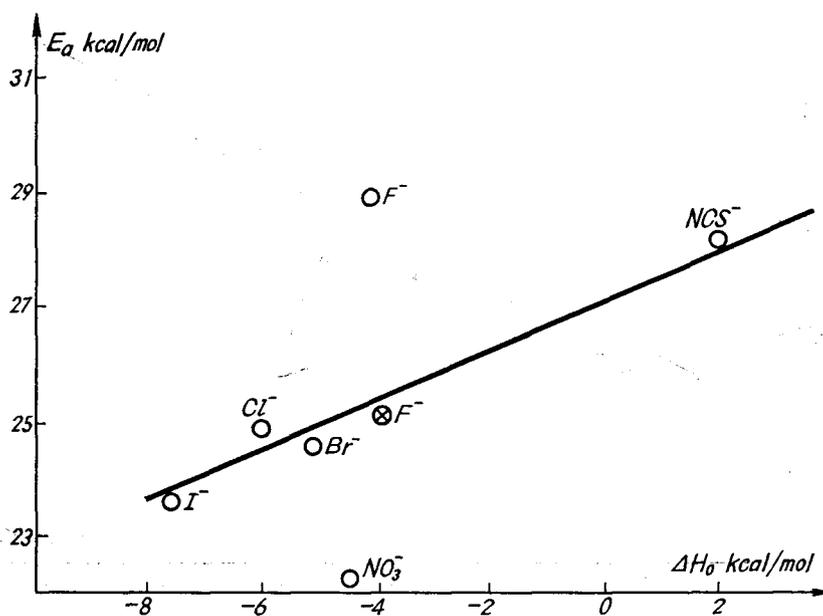


Fig. 6.

The Theory of the Kinetics of the Ligand Substitution Processes

it can be seen that the fluoride complex does not belong to the general series. It was found from estimates based on equation (3) that E_a in this case (~ 65 kcal/mol) greatly exceeds the average value for the series (~ 45 kcal/mol). If E_a for the fluoride complex is calculated using the latter value of E_a , the corresponding point falls on the graph of Fig. 6.

The considerable change of ΔS^\ddagger and ΔS_0 along the series means that the value of the Brönsted coefficient α , determined from the dependence of $\log k$ on $\log K$, may differ noticeably from the value determined from the dependence of E_a on ΔH_0 . Probably, this situation is found in the aquation reactions of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ complexes. Thus the coefficient α characterizing the relation between the logarithms of the rates and the equilibrium constants in the aquation reactions is found to be close to 1 (Fig. 7.). We can assume however that if the Brönsted coefficient is obtained from the dependence of E_a on ΔH_0 , it will have approximately the same value as for the aquation reactions of $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{2+}$ complexes (for the latter series, the value of α determined from the dependence of E_a on ΔH_0 is very close to the value determined from the relations between $\log k$ and $\log K$). The

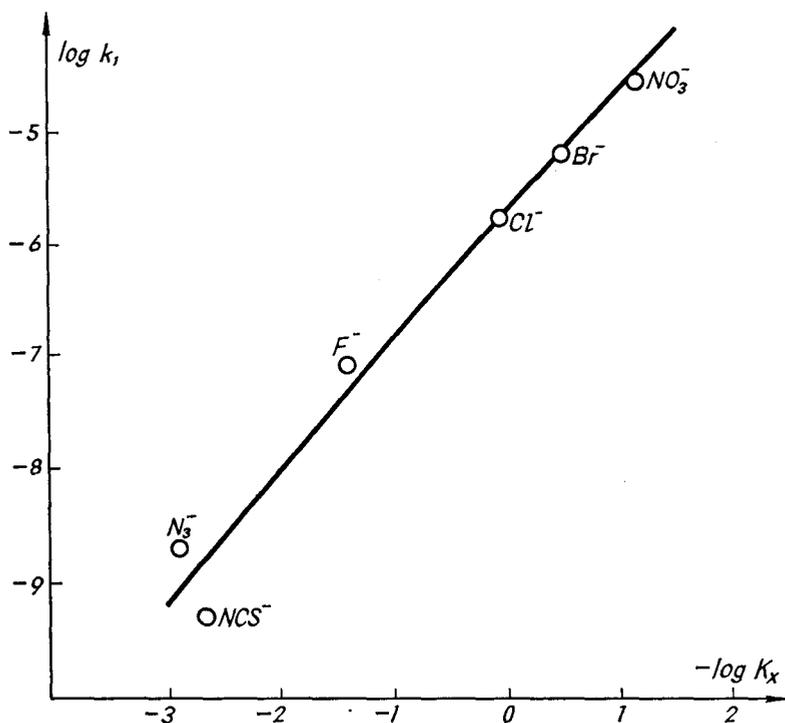


Fig. 7.

assumption is justified by the fact that the estimated energies of activation of the Co(III) reactions, using, the kinetic parameters of the Cr(III) reactions, give good agreement with experiment, thus implying that the values of the two sets of parameters are very close to each other.

The difference in experimental values of α for aquation of the $[\text{Cr}(\text{H}_2\text{O})_5\text{X}]^{+2}$ and $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ complexes was used, in our opinion wrongly, to deduce different types of activated complex for the two series⁴²⁾. According to the theory presented above, the transition states must be the same for both the chromium and cobalt series. Therefore, we found that it is more correct to investigate (where possible) the correlation between E_a and ΔH_0 and to consider separately the changes in entropy of activation and reaction.

Equations (2) also predict a relation between the rate constants of aquation reactions of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ complexes and the energies ($h\nu$) of the first band of the absorption spectrum in UV-range (provided that the values of other kinetic parameters can be considered approximately constant). Such a relationship has been observed experimentally⁴²⁾ and an analysis of the data shows that the assumption of constant E_a , E_r^x and E_r^{aq} is well obeyed, except for $\text{X}^- = \text{F}^-$ of N_3^- . Assuming that the energy of hydration of the $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ complexes does not depend on X (*i.e.* the sizes and charge distribution of the complexes are approximately constant), the change in the heat of the aquation reactions $\delta(\Delta H_0)$ with X^- is given by

$$\delta(\Delta H_0) = \delta(\Delta H_X^h) + \delta(\Delta H_X^a) \quad (4)$$

where $\delta(\Delta H_X^h)$ is the change of the heat of hydration of ion X^- and $\delta(\Delta H_X^a)$ the corresponding change of the bond energy Co-X. As this relation is linear, it follows that the values of change monotonously, this indicated that in the given series of reactions, as well the Co-X bond energy as the heat of hydration of X^- decrease in absolute value. In general this correlation is not obvious, as the variation in the heats of bond formation depends on both X and the metal properties. If the value of one of the parameters $\delta(\Delta H_X^h)$ or $\delta(\Delta H_X^a)$ increases and the other one decreases, a minimum should be observed in the plot of $\log k$ against $h\nu$, provided that the range of reaction heats is wide enough.

We now consider, in terms of the theory given above, some experimental data concerning the kinetics of aquation of $[\text{Cr}(\text{NH}_2\text{R})_5\text{Cl}]^{2+}$ complexes, where $\text{R} = \text{H}$, CH_3 , C_2H_5 , $n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$ ²³⁾ (Table 6). If the difference in the bond energies of M-OH₂ and M-X in the complexes is denoted by $\delta(\Delta H_{\text{M-O, M-X}})$, and the difference in hydration energy of $[\text{ML}_5\text{H}_2\text{O}]^{2+}$ and $[\text{ML}_5\text{X}]^{2+}$ (where $\text{M} = \text{Cr(III)}$, $\text{L} = \text{NH}_2\text{R}$) by $\delta(\Delta H_{\text{comp}}^h)$, then the change in

The Theory of the Kinetics of the Ligand Substitution Processes

TABLE 6. The kinetic and thermodynamic parameters of aquation reactions*) $[\text{Cr}(\text{NH}_2\text{R})_5\text{X}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Cr}(\text{NH}_2\text{R})_5\text{H}_2\text{O}]^{+3} + \text{X}^-$

R	E_a kcal/mole	a Å	E_s kcal/mole	ΔH_0^{exp} kcal/mole	ΔH_0^{exp} kcal/mole
H	23.3	2.5	45.5	-6.0	} ~8
CH ₃	27.0	5.4	43.0		
C ₂ H ₅	27.0	6.5	43.5		
C ₃ H ₇	27.0	7.7	44.0		
C ₄ H ₉	27.0	8.9	44.5		

*) at 25°C in aqueous solution.

reaction heat $\delta(\Delta H_0)$ corresponding to change in R equals :

$$\delta(\Delta H_0) = \delta(\Delta H_{\text{M-O, M-X}}) + \delta(\Delta H_{\text{compl}}^{\text{X}}) \quad (5)$$

From equation (2), putting $r = a + b$, it is found that E_s is practically constant (Table 6). As obviously also the values of the parameters E_r^{X} and E_r^{aq} are constant for a given X, it follows that practically all the change in the energy of activation throughout a series of reaction arises from a change in the heat of reaction $\delta(\Delta H_0)$. Considering a given series R, we can conclude that an abrupt change in activation energy takes place when H in L is replaced by CH₃, while the energy of activation remains nearly constant when the methyl group is replaced by higher aliphatic radicals. It was estimated that a substitution of H by CH₃ leads to a change in ΔH_0 of about ~ 14 kcal/mol, which apparently is the maximum value of $\delta(\Delta H_0)$. (Calculation of the heat of reaction from the energy of activation is considerably less accurate than the reverse calculation). The constancy of the reaction heat when replacing CH₃ by higher radicals implies, that the relative increase in the difference of the hydration energies of the $[\text{ML}_5\text{H}_2\text{O}]^{+3}$ and $[\text{ML}_5\text{X}]^{+2}$ complexes (decrease in the absolute value) is compensated by a decrease in the bond energies of M-OH₂ and M-X, *i.e.* $\delta(\Delta H_{\text{compl}}^{\text{X}}) = -\delta(\Delta H_{\text{M-O, M-X}})$. Apparently a more realistic situation is that one when the main change in the bond energy difference M-OH₂ and M-X occurs when replacing H by CH₃ while this difference remain nearly constant, when CH₃ is replaced by higher radicals. This assumption implies that the heat of reaction along a series of radicals from CH₃ to C₄H₉ does not stay constant, but increases somewhat, although not as sharply as when going from H to CH₃. Thus the energy of activation does not change and therefore, when going from CH₃ to C₄H₉ E_s must change somewhat. The latter change is difficult to estimate theoretically within the framework of a tractable model.

E. D. GERMAN and R. R. DOGONADZE

Acknowledgement

The authors are grateful to Dr. O. N. Temkin and Dr. M. N. Vargaftic for useful discussions.

References

- 1) P. G. ASHMORE, *Catalysis and Inhibition of Chemical Reactions*, Lond., Butherworth, 1963.
- 2) V. G. LEVICH, *Advances in Electrochemistry and Electrochem. Eng.* **4**, 249 (1966); *Phys. Chem.*, Vol. **9 B**, p. 985 (1970).
R. R. DOGONADZE and A. M. KUZNETSOV, *Itogi Nauki, Electrochim.* 1967, Moscow, 1969.
- 3) R. R. DOGONADZE, in *Reactions of Molec. at Electrodes*, ed. by N. Hush, Wiley Lond., 1971.
- 4) M. A. VOROTYNTSEV and A. M. KUZNETSOV, *Vestnik Mosk. Gos. Univ., Ser. Phys.*, **2**, 146 (1970).
- 5) D. ADAMS, *Metal-Ligand Vibration*, N. Y. (1968).
- 6) R. R. DOGONADZE, A. M. KUZNETSOV and V. G. LEVICH, *Dokl. Acad. Nauk*, **188**, 383 (1969).
- 7) B. MOROSIN, *Acta Cryst.*, **21**, 280 (1966).
- 8) R. A. MARCUS, *J. Chem. Phys.*, **24**, 966 (1956).
- 9) T. SWADDLE and E. KING, *Inorg. Chem.*, **4**, 532 (1965).
- 10) T. SWADDLE and G. GUSTALLA, *Inorg. Chem.*, **7**, 1915 (1968).
- 11) C. F. HALE and E. KING, *J. Phys. Chem.*, **71**, 1779 (1967).
- 12) K. SCHUG and E. KING, *J. Am. Chem. Soc.*, **80**, 1089 (1958).
- 13) F. A. GUTHRIE and E. KING, *Inorg. Chem.*, **3**, 916 (1964).
- 14) J. H. ESPENSON and E. KING, *J. Phys. Chem.*, **64**, 380 (1960).
- 15) J. H. ESPENSON, *Inorg. Chem.*, **3**, 968 (1964).
- 16) T. SWADDLE, *J. Am. Chem. Soc.*, **89**, 4338 (1967).
- 17) M. ARDON and N. SUTIN, *Inorg. Chem.*, **6**, 2268 (1967).
- 18) C. POSTMUS and E. KING, *J. Phys. Chem.*, **59**, 1208, 1216 (1955).
- 19) T. SWADDLE and E. KING, *Inorg. Chem.*, **3**, 234 (1964).
- 20) T. P. JONES and J. K. PHILLIPS, *J. Chem. Soc., A*, 674 (1968).
- 21) S. C. CHAW and K. Y. HUI, *Austr. J. Chem.*, **20**, 893 (1967).
- 22) A. ROGERS and P. J. STAPLES, *J. Chem. Soc.*, 6834 (1965).
- 23) M. PARRIS and W. J. WALLACE, *Can. J. Chem.*, **47**, 2257 (1969).
- 24) M. A. LEVINE *et al.*, *J. Am. Chem. Soc.*, **83**, 2453 (1961).
- 25) N. DUFFY and J. EARLEY, *J. Am. Chem. Soc.* **89**, 272 (1967).
- 26) S. HASHIMOTO, *Bull. Chem. Soc. Japan*, **32**, 945 (1959).
- 27) D. L. GAY and G. C. LALOY, *J. Chem. Soc. A*, 1179 (1966).
- 28) A. W. ADAMSON and R. G. WILKINS, *J. Am. Chem. Soc.*, **76**, 3379 (1954).
- 29) F. MONACELLI, *Ric. Sci.*, **37**, 781 (1967).

The Theory of the Kinetics of the Ligand Substitution Processes

- 30) S. C. CHAN, J. Chem. Soc., 2375 (1964).
- 31) R. PEARSON, C. BOSTON and F. BASOLO, J. Phys. Chem., **59**, 304 (1955).
- 32) G. S. LALOR and E. MOELWYN-HUGHES, J. Chem. Soc., 1560 (1963).
- 33) G. C. LALOR and G. W. BUSHNELL, J. Chem. Soc. A, 2520 (1968).
- 34) S. C. CHAN and F. LEH, J. Chem. Soc. A, 292 (1967).
- 35) H. TAUBE, J. Am. Chem. Soc., **82**, 524 (1960).
- 36) A. HAIM and H. TAUBE, Inorg. Chem., **2**, 1199 (1963).
- 37) F. BASOLO and R. PEARSON, *Mechanisms of Inorganic Reactions*, N. Y. (1967).
- 38) W. E. JONES, R. B. JORDAN and T. W. SWADDLE, Inorg. Chem. **8**, 2504 (1969).
- 39) T. W. SWADDLE and G. GUSTALLA, Inorg. Chem., **8**, 1604 (1969).
- 40) S. C. CHAN, Austr. J. Chem., **20**, 61 (1967).
- 41) A. J. POË and K. SHAW, Chem. Comm., 52 (1967).
- 42) C. H. LANGFORD and H. B. GRAY, *Ligand Substitution Processes*, Benjamin, N. Y., 1966.