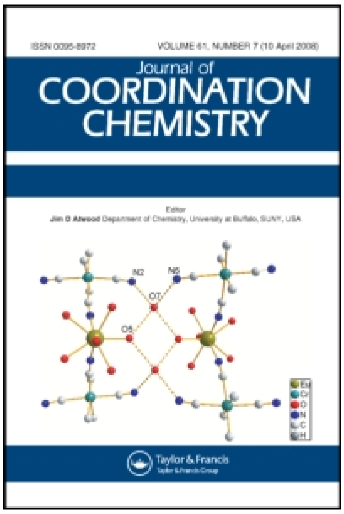

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STERIC EFFECTS IN REACTIONS OF METAL COMPLEXES. THE LIGAND SUBSTITUTION PROCESSES

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STERIC EFFECTS IN REACTIONS OF METAL COMPLEXES. THE LIGAND SUBSTITUTION PROCESSES.

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A model for the calculation of the activation energy for the ligand substitution processes in the metal complexes, occuring in the polar solvents, is suggested. The model takes into account sharp repulsion between the ligands at small distances. The structure of the transition state is analysed depending on the sharp repulsion distance between the ligands, symmetry factor α, and position of the incoming group with respect to the outgoing group (cis or trans). It is shown that for certain values of the parameters cis-substitution may be preferable than trans-substitution.

KEY WORDS: Steric Effects, Transition State, Activation Energy, Potential Energy Surface, Kinetics Ligand Substitution Processes.

INTRODUCTION

For correct quantum-mechanical calculation of the rate constant of the elementary act of a chemical reaction first and foremost information on the potential energy surface of the system under investigation is required. Because of the computational difficulties which arise in the calculation of the complex dynamical systems, especially those containing heavy elements, when analysing the reactivity of coordination compounds it is usual, instead of calculating the entire surface, to consider the structure and energy of the transition state of the reacting particles for which the choice of geometry is dictated mainly by intuitive considerations. But reliable calculations of just one such structure demand considerable expenditure of labour and computer time. So in the majority of cases they are restricted to qualitative or semi-quantitative analysis of changes in the electronic energy of the system caused by change in the non-bonding electron configuration of the central atom, the nature or symmetry of its surroundings and the position of the molecular orbitals of the complex. It is not difficult to see that this approach ignores the entropy contribution to the free energy of activation, the dynamical role of the solvent on the reaction rate, and the role of steric effects.

In this and subsequent reports we examine the significance of the above factors in the reactions of coordination compounds using the quantum-mechanical theory of reaction kinetics.[1–3]

The quantum mechanical theory which we use enables us to take account of the dynamical effect of the solvent on the kinetics of processes in polar media, and also give a quantitative description both of the structure of the transition configuration and the pre-exponential factor without having detailed information on the potential energy surface of the system in question. Using quantum theory a qualitative investigation has been made of several substitution reactions in octahedral and quadratic complexes of transition metals.[4–6] This work attempts to explain the role of steric factors in substitution reactions in octahedral complexes which proceed by an associate mechanism.

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ACTIVATION ENERGY AND TRANSITION STATE

(a) *Qualitative Examination*

In analysing the elementary act of reactions which take place in solutions it is essential to consider the potential energy surface as a function of a set of normal coordinates, {q}, which describe the state of the solvent, and a set of coordinates (intra and intermolecular), {**R**}, which characterize the reactants in the initial state and the products in the final state.[1,2] Accordingly, the total activation energy of the substitution process can be represented as a sum of two components, one of which is related with the formation of the transition configuration {q}* along the coordinates {q}, and the other with the formation of the transition configuration {**R**}* along the coordinates {**R**}.

Using the polarization vector $\mathbf{P}$ ($\equiv \{q\}$) to describe the state of the polar medium one can write for the transition state which is intermediate between the initial ($\mathbf{P}_{oi}$) and final ($\mathbf{P}_{of}$)

$$\mathbf{P}^* = \mathbf{P}_{oi} + \alpha(\mathbf{P}_{of} - \mathbf{P}_{oi}) \qquad (1)$$

where α is the factor† describing the deviation of the transition configuration from the initial (final) one. If $\alpha = 0$, for example, then $\mathbf{P} = \mathbf{P}_{oi}$, and if $\alpha = 1$, then $\mathbf{P} = \mathbf{P}_{of}$. It is much more complicated to calculate the coordinates {**R**}* of the transition configuration. This is due to the following reasons:

1. The shape of the intermolecular potential of interaction between the incoming group and the central ion of the complex depends not only on the distance between them, but on the coordinates of the other ligands (at least two). In fact in the case when the effective diameter‡ of the reaction centre of the incoming group is greater than the difference between the equilibrium distance l (see Figure 1) between the centres of neighbouring ligands and the sum of the Van der Waals radii of rigid frames, this group would experience a sharp repulsion from ligands (when incoming into the complex) even at distances considerably greater than equilibrium length of the bond, if l is assumed to be fixed. It is obvious that sharp repulsion begins at smaller distance between the reaction centre and the central ion, if l is increased either by deformation or by stretching of the corresponding bonds.† When l is sufficiently large so that the free space between the ligands is at least equal to the diameter of the incoming group, the region of sharp repulsion begins at distances which do not exceed the length of the metal–ligand bond.

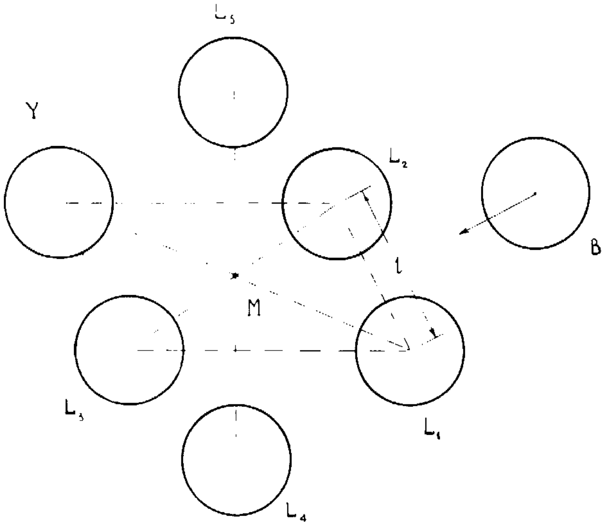

FIGURE 1 The model of an octahedral complex and incoming group. The circles represent the frames of the ligand atoms. *l* is the equilibrium distance between the frames.

2. Because of the short range forces of repulsion the movement of the particles obeys the classical laws only at sufficiently large distances, where the potential changes smoothly. At the same time at shorter distances (less than the sum of the Van der Waals radii of the rigid frames of the atoms), when the repulsive potential varies very sharply, the movement of these particles cannot be regarded as calssical. To check the validity of this let us examine the potential $u(R) = (m\omega^2/8)(R - a^2/R)^2$ which can be used for an approximation of the profile of the potential energy surface along the intermolecular coordinate of the incoming group (for fixed values of other coordinates). Here m is the reduced mass, ω is the frequency of particle oscillation near the minimum $R = a$. This potential contains the left steep branch which describes sharp repulsion at short distances, and the right smooth branch (Figure 2). The exact quantum-statistical distribution function on the coordinates, $\Phi(R)$, calculated for the given potential

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† As shown in [7] α coincides with the symmetry factor (see formula (10)).

‡ It is possible to use the values of the particles' Van der Waals radii to evaluate their effective dimensions.

† As estimates show, the ratio E_{def}/E_{str} for the expenditure of energy when l is increased by Δl via deformation of the bond angle and by stretching of the bonds is approximately equal to the ratio of the force constants k_{def}/k_{str}.

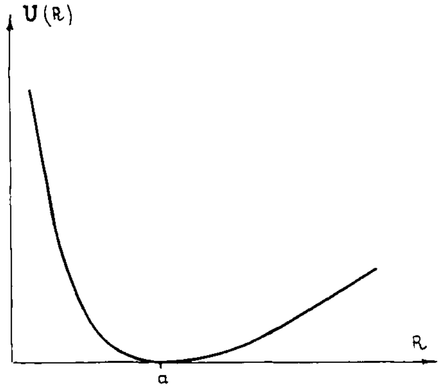

FIGURE 2 The potential curve, $U(R)$, involving the left steep and right smooth branches.

has the form

$$\Phi(R) = \frac{m\omega R}{\hbar} \exp\left[\frac{\hbar\omega\lambda}{2kT} - \frac{m\omega R^2}{2\hbar} \operatorname{cth} \frac{\hbar\omega}{2kT}\right] \cdot I_\lambda\left(\frac{m\omega R^2}{2\hbar sh[\hbar\omega/2kT]}\right), \qquad (2)$$

$$\lambda = \tfrac{1}{2}[1 + m\omega^2 a^2/\hbar]$$

where I_λ is the Bessel function of imaginary argument. In real conditions the amplitude of zero-point vibrations, $[\hbar/m\omega]^{1/2}$, is considerably less than a, i.e. sharp repulsion begins quite a long way from the minimum. This means that $\lambda \approx m\omega a^2/2\hbar \gg 1$. Taking into account that the oscillation frequency of a particle's centre of gravity in a liquid always satisfies the condition $\omega \ll kT/\hbar$, formula (2) can be greatly simplified using these assumption

$$\Phi(R) \cong [m\omega^2/2\pi kT]^{1/2} \cdot \exp\left[-\frac{U(R)}{kT}\right], \qquad R \gg \tilde{R} \equiv \frac{a}{2}[\hbar\omega/kT]^{1/2} \qquad (3)$$

$$\phi(R) \cong \frac{c^2}{|\tilde{p}|} \cdot \exp\left[-\frac{2}{\hbar}\int_{\mathrm{R}}^{\tilde{\mathrm{R}}} |\tilde{p}|\, \mathrm{d}R\right] \cdot \exp\left[-\frac{U(R)}{kT}\right], \quad R \ll \tilde{R} \qquad (4)$$

where the designations

$$c^4 = \frac{m\omega^3 a^2}{4\pi\hbar}, \qquad |\tilde{p}| = \sqrt{2m[U(R) - U(\tilde{R})]}$$

are introduced.

From (3) and (4) it follows that for a large enough distance between the particles ($R \gg \tilde{R}$) and for smooth interaction potential the coordinate distribution function coincides with the Boltzmann distribution, i.e. it is determined by classical statistics: the probability of approaching the small distances, however, is dependent on two factors, the classical movement to the point $\tilde{R}$ (see the last factor in (3)) and subsequent tunneling from point $\tilde{R}$ to point R (see the Gamov factor in eq. (4)).

The possibility of quantum and classical behaviour of a degree of freedom depending on the relation between the quantum energy ($\hbar\omega$) and kT was pointed out.[7,8] The fact that as the incoming particle approaches the complex the nature of its movement changes from classical to quantum along the same coordinate was a specific feature of the reactions investigated. This is peculiar to movement not only along the intermolecular potentials, but also for the movement along the intramolecular potentials for large deformation of the bond angles; in both cases harmonic approach does not hold.

The above difficulties in determining $\{\mathbf{R}\}^*$ can, however, be overcome to some extent by using several simplfying suppositions. Specifically, one can approximate the steep branch of the potential which corresponds to quantum movement by an infinite potential barrier. In fact this approximation enables one to use the classical description of particle movement in the system investigated. Another important simplification is based on the fact that the stretching force constant of skeletal ligand vibrations (k_{str}) for many transition metal complexes is considerably greater than the bending force constant (k_{def}).[9] This results in the fact that in the transition state the coordinate R^*_{B} of the incoming group in relation to the central ion almost coincides with its final equilibrium position $R^{f}_{0\,\mathrm{B}}$, and the coordinate R^*_{Y} of the outgoing group almost coincides with the initial equilibrium position $R^{i}_{0\,\mathrm{Y}}$. This can be seen from the example of a symmetrical substitution reaction. In fact, from considerations of microscopic reversibility it follows that in the transition state the incoming and outgoing groups are located at the same distance from the central atom. The size of this distance is determined by the optimum energy expenditure on stretching of the $M-Y$ bond and on deformation of the bond angles in the initial complex needed, as pointed out already, to form the free space for the incoming group B. The stretching of the $M-Y$ bond is an alternative for the deformation of bond angles. But, as actual evaluation show†, for $k_{\mathrm{str}}/k_{\mathrm{def}} \gg 1$

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†It is assumed that the coefficient α is not strictly equal to 0 or 1.

deformation of the bond angles of the complex and freeing of the space needed for the incoming group is energetically more favourable. Thus in the transition state all the ligands of the complex, including the outgoing ligand Y, and the incoming particle B are all at almost the same distance from the central ion. So the task of determining $\{\mathbf{R}\}^*$ comes down to calculating the angular coordinates of the particles $\{\mathbf{R}/R\}^*$ in the transition state.

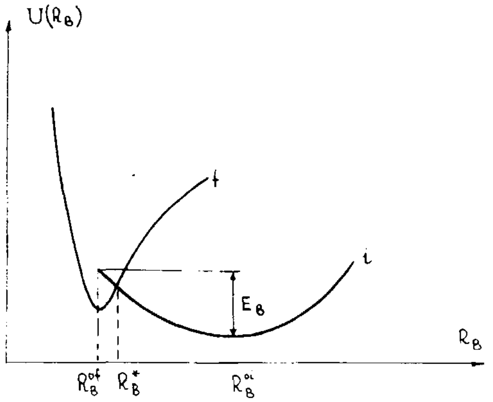

FIGURE 3 The profile of the potential surfaces along the R_B coordinate.

It follows that the contribution to the activation energy caused by the formation of a transition configuration along coordinates $\{\mathbf{R}\}$ involves two components. The first, E_B, represents the energy required for the introduction of the incoming group B from the solvent to the complex. The other component, E_{def}, describes the deformation energy of the bond angles in the complex from the initial equilibrium values to the values in the transition configuration. Thus the total activation energy of the process E_a is the sum

$$E_a = E_{sol} + E_B + E_{def} \tag{5}$$

The first component in (5) is equal to[1,2]

$$E_{sol} = \alpha^2 E_s$$

where E_s is the reorganisation energy of the solvent. This result also follows directly from (1), if one bears in mind that the energy of a system with polarization $\mathbf{P}^*$ is proportional to $(\mathbf{P}^*)^2$. The component E_B is determined by the shape of the intermolecular interaction potential and the value of displacement from the initial to the final equilibrium position (Figure 3). It is virtually constant for a reaction series with the same reaction centre. The component E_{def} will be calculated below in various models. It is not difficult, however, to investigate qualitatively how it changes with α.

Let us consider attack along the edge of the octahedron. We can then restrict ourselves to analysing the positions of particles in the plane containing four ligands and the incoming group B. It is clear that when the particle B is inserted into the complex the nearest ligands to it are forced to move by such an angle χ that the distance between the centre of each of these ligands and the centre of B is at least equal to the sum of the radii of their rigid frames (state I, Figure 4). The magnitudes of the remaining three angles in the initial equilibrium position (assuming that the ligands are identical) are equal $2(\pi - \chi)/3$,

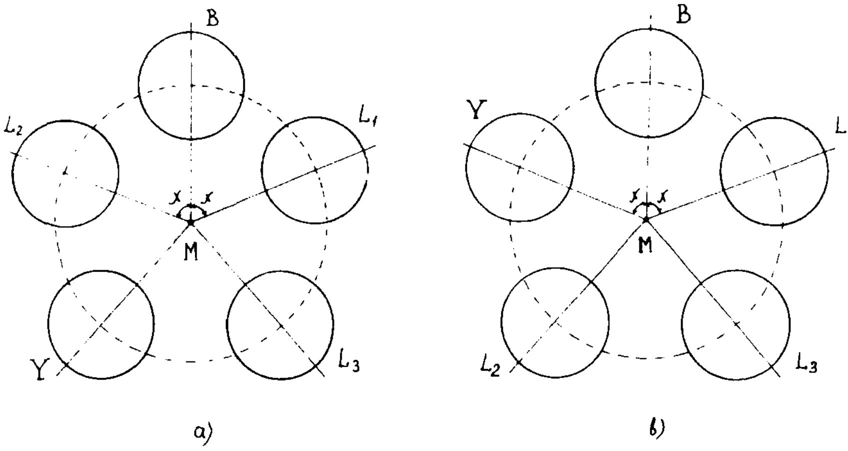

FIGURE 4 The states I; scheme of the ligand arrangement in the plane of the incoming and outgoing groups. (a) trans-substitution, (b) cis-substitution.

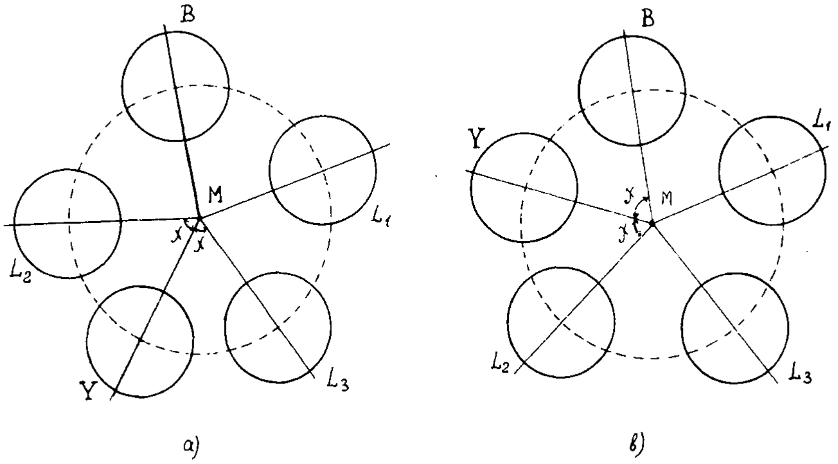

FIGURE 5 The states II; scheme of the ligand arrangement in the plane of the incoming and outgoing groups. (a) trans-substitution, (b) cis-substitution

both in case of trans-substitution, and when the outgoing group is in a cis-position in relation to B. We shall use II to denote the states in which the group B is chemically bonded with the metal, the M–Y bond is broken, but Y is still in the complex (Figure 5a, b). In these two states the angles between Y and the neighbouring ligands are equal to χ, and the angles between the remaining ligands are $2(\pi - \chi)/3$. As can be seen from Figure 5a, b the II states are different for cis- and trans-substitution. It is not difficult to calculate that the difference in energies of states I and II for trans-substitution, ΔE_{trans}, and for cis-substitution, ΔE_{cis}, are $2k_{\text{def}}(2\pi - 5\chi)/9$ and $k_{\text{def}}(2\pi - 5\chi)/9$ respectively, where k_{def} is the bending force constant. Since the transition state coincides with state I for $\alpha = 0$ and with II for $\alpha = 1$, the magnitudes ΔE_{trans} and ΔE_{cis} describe the change in the contribution of E_{def} to total activation energy for transition from $\alpha = 0$ to $\alpha = 1$. As evaluations show, values of χ for typical atoms are close to $2\pi/5$. For N and O atoms, for example, the values of χ calculated using the Van der Waals radii[10] are ~70°. Consequently for these χ the changes in ΔE_{trans} and ΔE_{cis} are insignificant. In other words when the atoms have rigid frames with quite large radii, the configuration of the transition state with respect to the angular coordinates of the ligands is almost independent on the reaction heat, i.e., the component E_{def} varies slightly with changing α.

This qualitative analysis may be proved by quantitative calculations for various specific forms of the interaction potential.

(b) *Calculation of the Activation Energy*

In the model outlined above (where the movement of all particles in the system is classical) the activation energy, E_a, is determined by the position of the saddle point on the multidimensional adiabatic surface U_-, which is a function of the coordinates of the solvent, all the ligands and the central ion. Bearing in mind that the energies of the excited electron states are large, to construct this surface it is possible, as an approximation to restrict oneself to basic electron terms (i.e. to the lower potential energy surfaces). The first one, U_i, is the sum of the potential energy of the solvent, $U_i^s(\{q\})$, the intramolecular energy of the complex ML_5Y, $U_i^{\text{compl}}(\mathbf{R}_{L_1}, \mathbf{R}_{L_2}, \ldots \mathbf{R}_Y)$, and the energy of interaction of the complex ML_5Y as a whole with incoming group B (with no change in electron wave functions), $\nu_i(\mathbf{R}_B)$, in the initial state, i.e.

$$U_i = U_i^s(\{q\}) + U_i^{\text{compl}}(\mathbf{R}_{L_1}, \mathbf{R}_{L_2}, \ldots \mathbf{R}_Y) + \nu_i(\mathbf{R}_B) + I_i \qquad (7)$$

where I_i is the minimum magnitude of U_i for equilibrium values of the coordinates. The second potential energy surface, U_f is the sum of the potential energy of the solvent, $U_f^s(\{q\})$, the intramolecular energy of the complex ML_5B, $U_f^{\text{compl}}(\mathbf{R}_{L_1}, \mathbf{R}_{L_2} \ldots \mathbf{R}_B)$ and the energy of interaction, $\nu_f(\mathbf{R}_Y)$, of the complex ML_5B as a whole with the outgoing group Y in the final state, i.e.,

$$U_f = U_f^s(\{q\}) + U_f^{\text{compl}}(\mathbf{R}_{L_1}, \mathbf{R}_{L_2} \ldots \mathbf{R}_B) + \nu_f(\mathbf{R}_Y) + I_f \qquad (8)$$

Then if V is the splitting energy of the states U_i and U_f in the region of the transition configuration, one can obtain the following expression for the adiabatic potential energy surface U_-

$$U_- = \tfrac{1}{2}(U_i + U_f) - \tfrac{1}{2}[(U_i - U_f)^2 + 4V^2]^{1/2} \qquad (9)$$

In accordance with [1, 11] the coordinates $\{\xi_x^*\}$ of the saddle point ($\{\xi_x\}$ includes both the coordinates of the solvent, $\{\mathbf{q}\}$, and the coordinates of the ligands $\mathbf{R}_{L_1}, \mathbf{R}_{L_2}, \ldots \mathbf{R}_Y, \mathbf{R}_B$) on the surface U_- can be found by solving the following equations

$$(1 - \alpha_{ad})\frac{\partial U_i(\{\xi_x\})}{\partial \xi_x} + \alpha_{ad}\frac{\partial U_f(\{\xi_x\})}{\partial \xi_x} = 0 \qquad (10)$$

$$U_i(\{\xi_x\}) = U_f(\{\xi_x\}) + (2\alpha_{ad} - 1)[(U_i(\{\xi_x\}) - U_f(\{\xi_x\}))^2 + 4V^2]^{1/2} \qquad (11)$$

where α_{ad} is the symmetry factor of the adiabatic surface in the region of the transition configuration:

$$\alpha_{ad} = \frac{\partial U_-}{\partial(\Delta I)}, \quad \Delta I = I_f - I_i \qquad (12)$$

For the substitution reactions investigated here equations (10) and (11) should be used only for calculating the saddle point on the coordinates of the solvent and the angular coordinates of unsubstituted ligand of the complex, the incoming group B and the outgoing ligand Y, since, as has been pointed out above in qualitative analysis, the radial coordinates of particles in the transition state are approximately equal to the equilibrium length of the metal-ligand bond. Supposing that B attacks the edge and Y is in the trans-position, (7) and (8) can be written in the form

$$U_i = U_i^s(\{\mathbf{q}\}) + u(\omega_1 + \omega_2) + u(\omega_3) + u(2\pi - \omega_1 - \omega_2 - \omega_3 - \omega_4) + \nu(\omega_1) + \nu(\omega_2) + \nu_i(R_B^*) + I_i \qquad (13)$$

$$U_f = U_f^s(\{\mathbf{q}\}) + u(\omega_1) + u(\omega_2) + u(\omega_3 + \omega_4) + u(2\pi - \omega_1 - \omega_2 - \omega_3 - \omega_4) + \nu(\omega_3) + \nu(\omega_4) + \nu_f(R_Y^*) + I_f \qquad (14)$$

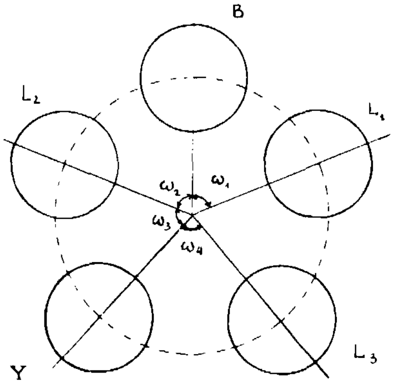

FIGURE 6 The scheme of the angles for trans-substitution.

In expressions (13) and (14) $u(\omega)$ represents the potential energy of interaction of the ligands with each other, and $\nu(\omega)$ the energy of repulsion between the chemically nonbonded particle (B in state I; Y in state II) and the nearest ligands of the complex to it (for designations of angles see Figure 6). The magnitude $\nu_i(R_B^*) \equiv E_B$ (see Figure 3) represents the contribution to the activation energy caused by the formation of the transition state on the radial coordinate of the B particle. The magnitude $\nu_f(R_Y^*) \equiv E_Y$ has a similar significance in relation to the corresponding coordinate for the same reaction, but in the reverse direction. For convenience we shall henceforward count the energy on the surface U_i from its minimum. Then (13) and (14) can be rewritten in the following way by introducing the designation $\Delta I = I_f - I_i$

$$U_i = U_i^s + u(\omega_1 + \omega_2) + u(\omega_3) + u(\omega_4) + u(2\pi - \omega_1 - \omega_2 - \omega_3 - \omega_4) + \nu(\omega_1) + \nu(\omega_2) + E_B \qquad (13')$$

$$U_f = U_f^s + u(\omega_1) + u(\omega_2) + u(\omega_3 + \omega_4) + u(2\pi - \omega_1 - \omega_2 - \omega_3 - \omega_4) + \nu(\omega_3) + \nu(\omega_4) + E_Y + \Delta I \qquad (14')$$

Within the model of dielectrical formalism the potential energy of the solvent has the form [12, 13]

$$U_i^s = (1/2)\sum_k \hbar\omega_\kappa q_k^2 \qquad (15)$$

$$U_f^s = (1/2)\sum_k \hbar\omega_\kappa (q_\kappa - q_{\kappa 0})^2 \qquad (16)$$

By substituting (13′), (14′), (15) and (16) in (10) we can find the saddle point on the coordinates of the solvent

$$q_\kappa^* = \alpha_{ad}\, q_{\kappa 0}, \qquad (17)$$

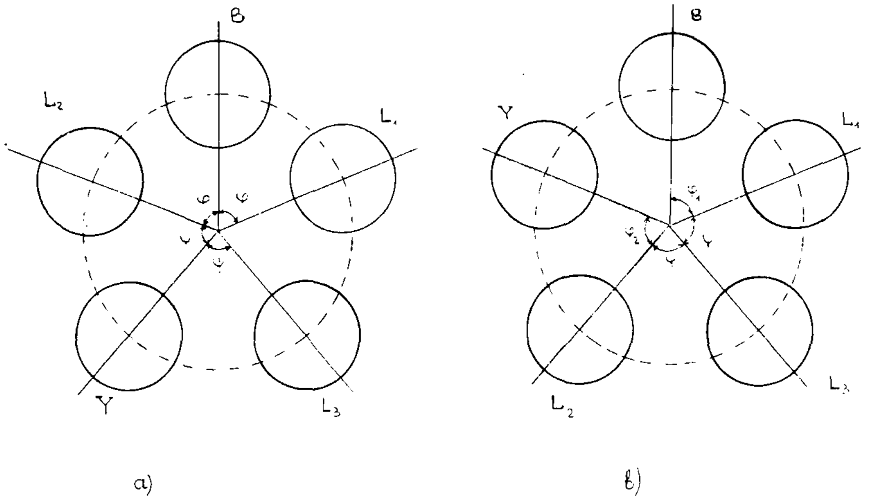

FIGURE 7 The transition states for an arbitrary α. (a) trans-substitution, (b) cis-substitution.

The saddle point on the angular coordinates, ω_m^*, in the case when the outgoing group Y is in the trans-position in relation to B, is determined by following equations

$$\begin{aligned}&(1-\alpha)\,u'(2\varphi)+\alpha u'(\varphi)+u'(2\pi-2\varphi-2\psi)\\&\quad+(1-\alpha)\,v'(\varphi)=0\\&\alpha u'(2\psi)+(1-\alpha)\,u'(\psi)-u'(2\pi-2\varphi-2\psi)\\&\quad+\alpha v'(\varphi)=0\end{aligned}\tag{18}$$

Here the subscript of the factor α is omitted to simplify the notation, and in place of ω_m we have introduced φ and ψ, whose significance is clear from Figure 7a.

If Y is adjacent to B (cis-substitution) (Figure 7b), then the set of equations for determining ω_m becomes

$$\begin{aligned}&\alpha u'(\varphi_1)+(1-\alpha)\,u'(2\pi-\varphi_2-2\psi)-u'(\psi)\\&\quad+(1-\alpha)\,v'(\varphi_1)=0\\&(1-\alpha)\,u'(\varphi_2)+\alpha u'(2\pi-\varphi_1-2\psi)-u'(\psi)\\&\quad+\alpha v'(\varphi_2)=0\\&\alpha u'(2\pi-\varphi_1-2\psi)+(1-\alpha)\,u'(2\pi-\varphi_2-2\psi)\\&\quad-u'(\psi)+v'(2\pi-\varphi_1-\varphi_2-2\psi)=0\end{aligned}\tag{19}$$

To solve eqs. (19) it is necessary to use some model approximations for the functions u and v. It is important that these model functions should take account of the sharp repulsion between the encountered particles at small distances (smaller than the sum of their Van der Waals radii). Therefore we choose the following model approximation for u and v.

$$\begin{aligned}&u(\omega)=\frac{k}{2}\left(\omega-\frac{\pi}{2}\right)^2\\&v(\omega)=0, \qquad \omega>x\\&u(\omega)=(\gamma/2)(\omega-a)^2+b\\&v(\omega)=(\gamma/2)(\omega-\chi)^2, \quad \omega<x\end{aligned}\tag{20}$$

Besides we shall put $k/\gamma\to 0$ in the final expressions, that means the use of the hards sphere approximation.

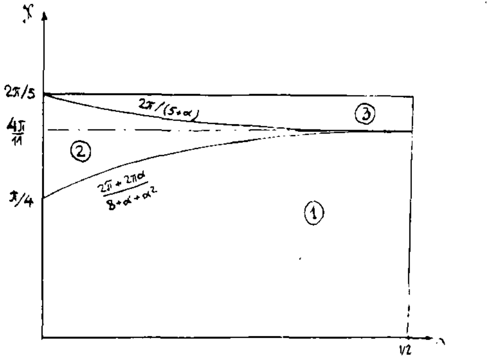

FIGURE 8 The notation $\chi-\alpha$ diagram for solution of eqs. (18).

TABLE I

Contribution to the activation energy, E_{def}, due to distortion of the complex by incoming group during the formation of the transition state for cis- and trans-substitution at various values of χ and α.[a]

E_{def}	χ	$\alpha = 0$	χ	$\alpha = \frac{1}{2}$
$E_{\mathrm{def}}^{\mathrm{trans}}$	$0 < \chi < \frac{\pi}{4}$	0	$0 < \chi < \frac{4\pi}{11}$	$\frac{k\pi^2}{22}$
	$\frac{\pi}{4} < \chi < \frac{2\pi}{5}$	$\frac{k\pi^2}{2}\,\frac{(4x-1)^2}{3}$	$\frac{4\pi}{11} < \chi < \frac{2\pi}{5}$	$\frac{k\pi^2}{2}(22x^2 - 16x + 3)$
$E_{\mathrm{def}}^{\mathrm{cis}}$	$0 < \chi < \frac{\pi}{4}$	0	$0 < \chi < \frac{\pi}{3}$	$\frac{k\pi^2}{2} \cdot \frac{x^2}{2}$
	$\frac{\pi}{4} < \chi < \frac{2\pi}{5}$	$\frac{k\pi^2}{2}\,\frac{(4x-1)^2}{3}$	$\frac{\pi}{3} < \chi < \frac{2\pi}{5}$	$\frac{k\pi^2}{2}\left(\frac{19}{2}x^2 - 6x + 1\right)$
$E_{\mathrm{def}}^{\mathrm{trans}} - E_{\mathrm{def}}^{\mathrm{cis}}$	$0 < \chi < \frac{2\pi}{5}$	0	$\chi \sim \frac{2\pi}{5}$	$25x^2 - 20x + 4$

[a] $x = \chi/\pi$

The final solutions† of eqs. (18) in the region of values $0 < \alpha < \frac{1}{2}$ (Figure 8) have the form: (the region $1 > \alpha > \frac{1}{2}$ is equivalent to the region $0 > \alpha > \frac{1}{2}$ for the reverse reaction)

$$1)\ 0 < \chi < \frac{2\pi(1+\alpha)}{8+\alpha-\alpha^2}; \quad \varphi^* = \frac{2\pi(1+\alpha)}{8+\alpha-\alpha^2},$$

$$\psi^* = \frac{2\pi(2-\alpha)}{8+\alpha-\alpha^2} \tag{21}$$

$$2)\ \frac{2\pi(1+\alpha)}{8+\alpha-\alpha^2} < \chi < \frac{2\pi}{5+\alpha}; \quad \varphi^* = \chi,$$

$$\psi^* = \frac{2\pi - 2\chi}{3+\alpha} \tag{22}$$

$$3)\ \frac{2\pi}{5+\alpha} < \chi < \frac{2\pi}{2}; \quad \varphi^* = \chi, \quad \psi^* = \chi \tag{23}$$

As was pointed out above $\chi \approx 2\pi/5$, which corresponds to the solution in the region 3. In this region the angles φ^* and ψ^* are independent of α, this confirms the statement made earlier on the basis of qualitative considerations that the structure of the transition configuration on angular variables is independent of the symmetry factor α. Solving Eqs. (19) for cis-substitution with arbitrary values of α is a more difficult task. Here the cases with $\alpha = 0$ and $\alpha = 1/2$ were the only two studied. For $\alpha = 0$ the angles φ^* and ψ^* are $\varphi^* = \pi/4$, $\psi^* = \pi/2$ if $0 < \chi < \pi/4$ and $\varphi^* = \chi$, $\psi^* = \frac{2}{3}(\pi - \chi)$ if $\pi/4 < \chi < \frac{2}{5}\pi$. The solutions for $\alpha = \frac{1}{2}$ have the form: $\varphi^* = (\pi - \chi/2)$, $\psi^* = (\pi/2)$, if $0 < \chi < \pi/3$ and $\varphi^* = \chi$, $\psi^*\ \frac{2}{3}(\pi - \chi)$, if $\pi/3 < \chi < 2\pi/5$.

By substituting in (13′) the coordinates of the saddle point for trans-substitution we obtain an expression for the activation energy in the form

$$\begin{aligned} E_a &= \alpha^2 E_S + E_B + u(2\varphi^*) + 2u(\psi^*) \\ &\quad + u(2\pi - 2\varphi^* - 2\psi^*) + 2v(\varphi^*) \\ &= \alpha^2 E_S + E_B + E_{\mathrm{def}}(Y) \end{aligned} \tag{24}$$

Solving equation (11) to determine α, assuming that $V \ll E_S$, leads to the following expression for α

$$\alpha = 1/2 + \frac{\Delta J}{2E_S}\left(1 + \frac{2V}{E_S} \cdot \frac{1}{[1 - \Delta J/E_S]^{1/2}}\right) \tag{25}$$

where

$$\Delta J = \Delta I + E_Y + E_B + E_{\mathrm{def}}(B) - E_{\mathrm{def}}(Y)$$

In expression (24) $E_{\mathrm{def}}(B)$ represents the expenditure of energy for deformation of the angles between the ligands needed to achieve the transition state like the magnitude $E_{\mathrm{def}}(Y)$ in the direct reaction. If

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†To simplify the calculations we shall assume that the angle χ is approximately the same for all ligands L, for B and Y.

$2V/E_S \ll 1$, the expression for E_a takes the form

$$E_a = E_B + E_{def}(Y) + \frac{(E_S + \Delta J)^2}{4E_S} - V\left[1 - \left(\frac{\Delta J}{E_S}\right)^2\right]^{1/2} \qquad (26)$$

The value of E_S in Eq. (26) in general depends on the direction of attack of the incoming group, since the redistribution of charges in the system is different for cis- and trans-substitution. This factor may play an important role in some reactions. But it is possible to neglect this factor if one assumes that the ligands which take part in the reaction have almost identical properties. The value of the energy E_B may be different depending on the nature of the incoming agent B, the central atoms and the ligands between which B enters. In the model examined it is assumed that E_B is independent of the direction of attack.

Consequently for the restrictions adopted the path of the reaction (cis or trans-substitution) is determined by the term E_{def}. Comparing the results shown in Table 1 one can make the following conclusions:

1) If the transition state is close to the initial one ($\alpha \sim 0$), steric factors have an affect on the direction of the process. In the class of reactions investigated this is hardly probable.

2) For values $\alpha \sim 1/2$ the expenditure due to steric factors for cis-substitution is less than for trans-substitution (apart from the case when χ is exactly to $2\pi/5$). Numerical evaluation shows that for reasonable values of χ and force constants (e.g. for $\chi = 1.9\pi/5$ and $k = 5.10^3$ dynes/cm) the ratio of rates for cis- and trans-substitution may reach ~15.

In order to clarify the role of steric factors in substitution processes we have used a considerably idealised model which does not take full account of the differences in the properties of ligands, the specific nature of the central ion, etc. By developing the theory it is possible in principle to take account of all these factors and we hope to analyse their influence on the kinetics of reactions in coordination compounds.

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