EFFECT OF PRESSURE ON THE RATE OF LIGAND DISPLACEMENT PROCESSES IN THE COORDINATION SPHERE OF METAL COMPLEXES

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Recently a number of works have appeared [1-5] which are devoted to an experimental study of the effect of pressure on the rate of ligand displacement processes in octahedral metal complexes.

$$ML_5X^{2+}+H_2O\rightarrow ML_5H_2O^{3+}+X^-. \quad (A)$$

Here it was shown that when $X\neq H_2O$ and M = Co or Cr, the rate of aquation reactions depends nonlinearly on the pressure, P:

$$\ln k_P=\ln k_0+BP+CP^2, \quad (1)$$

where k_0 is the value of the rate constant at atmospheric pressure, and B and C are empirical constants (P is the increase in pressure with reference to atmospheric; that is, P = p − 1). The constants B and C are connected with the activation volume at zero excess pressure, $\Delta V_0^{\neq}$, and with the compressibility coefficient of activation, $\Delta\beta^{\neq}$:

$$B=\left(\frac{d\ln k_P}{dP}\right)_{P=0}=-\frac{\Delta V_0^{\neq}}{kT}, \quad (2)$$

$$C=\frac{1}{2}\frac{d^2\ln k_P}{dP^2}=-\frac{d(\Delta V^{\neq})}{2dP}. \quad (3)$$

In connection with the development of the theory of reaction kinetics for ligand displacement in the coordination sphere of metal complexes [6], it is of interest to carry out a theoretical examination of this question.

According to the quantum theory of chemical reaction kinetics in polar media [7], the rate constant of reaction (A) taking place by an exchange mechanism (I) can be written in the form

$$k_p=\frac{kT}{h}\exp\left\{\ln\left(\varkappa\frac{\hbar\omega_i}{kT}v_i\right)-\left[E_{aq}+\frac{(E_s+\Delta J_P+E_x-E_{aq})^2}{4E_s}\right]\Big/kT\right\}\equiv\frac{kT}{h}\exp\left\{-\frac{\Delta G^{\neq}}{kT}\right\}, \quad (4)$$

where ω_i is the effective fluctuation frequency of the whole classical subsystem (that is, of the solvent and the other classical degrees of freedom along which the transition is taking place) for the initial state i; v_i is the reaction volume; E_s is the solvent reorganization energy; E_{aq} and E_x are the contributions to activation energy along the coordinates of the entering and leaving groups; and U_c is the coulombic interaction energy for the reaction products. The quantity ΔJ_p, which is the difference between the minimum values in terms of the final state, f, and the initial state at a constant external pressure P, is given by

$$\Delta J_P=\Delta J_0+P\Delta V=\Delta G-kT\ln\frac{\omega_i}{\omega_f}, \quad (5)$$

where ΔG is the change in free energy of reaction (A) at a constant pressure P, and ΔV is the change in molar volume of the system in the process of reaction (A).

We expand expression (4) into a series in powers of P up to the squared terms, introducing the following definitions:

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$$\gamma_0 \equiv \frac{\partial}{\partial P}(1/\varepsilon_0), \tag{6a}$$

$$\gamma_s \equiv \frac{\partial}{\partial P}(1/\varepsilon_s), \tag{6b}$$

$$E_s \equiv Q_s(1/\varepsilon_0 - 1/\varepsilon_s), \tag{7}$$

where ε_0 and ε_S are the optical and static dielectric permeabilities (writing the solvent reorganization energy in form (7) corresponds to using a model of the metallic spheres [8] to calculate this quantity in which the factor Q_S takes account of the geometric characteristics of the reacting particles). We now examine the dependence on pressure of all the parameters which enter into (4). In conformity with the estimates of Stranks [9], at the pressures customarily used in experiments, the complex ion can be considered practically incompressible as compared with the bulk of the solvent. This circumstance means that, in differentiating E_S with respect to pressure, the quantity Q_S should be considered constant. Due to the electrostriction effect, the solvent (water) molecules of the second coordination sphere are under a pressure of about 30 kbar [9]. Correspondingly the compressibility of the second coordinate sphere under the experimental conditions is slight as compared with that of the whole solvent volume. In connection with this, the effect of pressure on the activation parameters E_{aq} and E_X, which correspond to the entrance of a solvent molecule into the complex from the second sphere in the forward process, and of an X^- ion in the reverse one, can be neglected. For the same reason, the transmission coefficient $\varkappa$ can be assumed independent of pressure (if $\varkappa = 1$, this statement is rigorous), and so is the reaction volume, v_i. The dependence of ω_i on pressure may be omitted from consideration if the contribution from this effect to $\Delta V_0^{\neq}$ is small as compared with the whole activation volume; that is, if $kT\,|\,d\ln\omega/dP\,| \ll |\,\Delta V_0^{\neq}\,|$. At pressures $p \leqslant 3$-5 kbar (ordinarily used in experiments), this relationship corresponds to the condition $|\,d\ln\omega/d\ln P\,| \ll 1$, which, as estimates show, is fulfilled for the reactions under consideration. Differentiation of (4) using this approach, taking into account (6a), (6b), and (7), leads to the following expression for $\Delta V_0^{\neq}$:

$$\Delta V_0^{\neq} = \alpha(1-\alpha)(\gamma_0 - \gamma_s)Q_s + \alpha(U_c' + \Delta V). \tag{8}$$

In Eq. (8) we denote the symmetry factor* when P = 0 by α; this is given by

$$\alpha = {}^1/_2 + (\Delta J_0 + U_c + E_x - E_{aq})/2E_s = {}^1/_2 + \left(\Delta G_0 - kT\ln\frac{\omega_i}{\omega_f} + U_c + E_x - E_{aq}\right) \Big/ 2E_s, \tag{9}$$

where ΔG_0 is the value of ΔG when P = 0. Expression (8) is the correlation relationship between $\Delta V_0^{\neq}$ and the reaction volume ΔV for the reaction sphere (when the parameters Q_S, U_C, E_X, and E_{aq} can be considered only slightly variable) and may be compared with experimental results. As follows from (8), the correlation between the rate constants $\Delta V_0^{\neq}$ and ΔV is analogous to the correlation between the rate constant and equilibrium constant (with the same factor, α).

The second term in the expansion of (4) in powers of P is given by

$$\Delta\beta^{\neq} = [\alpha(1-\alpha)(\gamma_0' - \gamma_s') + \alpha'(1-2\alpha)(\gamma_0 - \gamma_s)]Q_s + \alpha'(U_c + \Delta V) + \alpha(U_c'' + \Delta\beta), \tag{10}$$

where

$$\alpha' = {}^1/_2 E_s[U_c' + (1-2\alpha)(\gamma_0 - \gamma_s)Q_s] + \Delta V/2E_s, \tag{11}$$

and $\Delta\beta = \partial^2(\Delta G)/\partial P^2$ is the compressibility coefficient of the reaction. According to (10) there is also a correlation characterizable by the factor α between the compressibility coefficient of the reaction and the activation coefficient.

To compare the theoretical expressions (8) and (10) with experiment, U_C should be assigned explicitly. In solutions of low concentration, one may neglect the effect of Debye shielding, representing U_C for the reaction products in the form $U_C = Z_{ML_5X} \cdot Z_X/R\varepsilon_S \equiv Q_C/\varepsilon_S$. Here $U_C' = Q_C\gamma_S$ and $U_C'' = Q_C\gamma_S'$. The quantity $\Delta\beta$, which is necessary for calculation of the compressibility coefficient of activation ($\Delta\beta^{\neq}$) can be measured experimentally. For a theoretical evaluation of $\Delta\beta$, one can use approximately the Born model. With this objective, we write ΔG as

$$\Delta G = \Delta E + \Delta G^s = \Delta E + \Delta G_{ML_5H_2O}{}^s + \Delta G_x{}^s - \Delta G_{H_2O}{}^s - \Delta G_{ML_5X}{}^s, \tag{12}$$

*The expression for the symmetry factor in form (9) corresponds to defining α_p at an arbitrary pressure as the derivative $\alpha_p = \partial(\Delta G^{\neq})/\partial(\Delta J_p)$. It can be shown that over a comparatively small range in ΔG the α_p factor so derived coincides with the experimentally observable factor $\alpha_p = \partial(\Delta G^{\neq})/\partial(\Delta G) = \partial(\Delta H^{\neq})/\partial(\Delta H)$.

TABLE 1. Activation Volume and Compressibility Coefficient of Activation for Displacement Reactions $ML_5X^{2+} + H_2O \rightarrow ML_5H_2O^{3+} + X^-$

ML_5	X	ΔV, $cm^3 \cdot mole^{-1}$	$\Delta V_0^{\neq}$, $cm^3 \cdot mole^{-1}$		$10^3 \Delta\beta^{\neq}$, $cm^3 \cdot mole^{-1} \cdot bar^{-1}$		Literature cited
			exp.	theor.	exp.	theor.	
$Cr(NH_3)_5$	Cl	−8.4	−10.6±0.3	−10.1	1.04±0.19	1.5	[5]
	Br	−7.2	−9.9±0.3	−9.5	1.04±0.14	1.36	"
	J	−6.0	−9.2±0.2	−8.9	0.96±0.13	1.24	"
	H_2O	0	−5.8±0.2		0±0.3		[3]
$Co(NH_3)_5$	Cl	−11.6	−9.9±0.5	−10.0	2.1±0.2	1.82	[4]
	Br	−10.8	−0.7±0.2	−9.3	2.0±0.2	1.73	"
	NO_3	−7.2	−5.9±0.4	−6.0	1.0±0.2	1.13	"
	NCS	—	−4.0±1.0	—	—		"
	H_2O	0	1.2±0.1		0±0.1		"

where ΔE is the difference in internal energies of ML_5H_2O and ML_5X, and ΔG^S is the free energy of solvation of the molecules participating in the reaction. In the framework of the Born model, the free energy of solvation is given by

$$\Delta G^s = [(Z^2_{ML_5H_2O} - Z^2_{ML_5X})/2r_K + Z_X^2/2r_X]/\varepsilon_s - \Delta G^*_{H_2O}, \quad (13)$$

(r_k and r_x are the radii of the complex and of the ion X^-). Neglecting the compressibility of the complex in comparison with the compressibility of the medium [9] and also neglecting the very small contribution to ΔG^S from solvation of the neutral molecule by H_2O, we find that

$$\Delta V = [(Z^2_{ML_5H_2O} - Z^2_{ML_5X})/2r_K + Z_X^2]\gamma_s = Q_B\gamma_s,$$
$$\Delta\beta = Q_B\gamma_s'. \quad (14)$$

Since, as is well known, calculation of solvation energies by the Born method gives too high values, calculation of $\Delta\beta$ within the framework of this model makes it possible to obtain only a qualitatively correct result. However, if the experimental value of ΔV is known, expression (14) can be used to find Q_B in calculations of the compressibility $\Delta\beta$. Here

$$\Delta\beta = (\gamma_s/\gamma_s')\Delta V. \quad (15)$$

Results of calculations of $\Delta V_0^{\neq}$ and $\Delta\beta^{\neq}$ by Eqs. (8), (10), and (15) are given in Table 1, together with experimental data. In calculating the activation parameters for ammine complexes of chromium the factor α can be assumed equal to about 0.5 on the basis of an analysis of the correlations between rate constant and equilibrium constant [10, 11]. In the case of displacement reactions in complexes $Co(NH_3)_5X$, the factor α is close to unity [12] ($\alpha \sim 0.9 \pm 0.1$). The theroetical values of $\Delta V_0^{\neq}$ and $\Delta\beta^{\neq}$ for ammine complexes of cobalt which are given in Table 1 were obtained at $\alpha = 0.9$. According to the results of [6], the quantity E_S and the distance R were taken as equal to about 40 kcal/mole and about 7 Å, respectively. Values of the constants γ_0, γ_S, and their derivatives were taken from the work of [13, 14].

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