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Abstract

Full Text

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ON SOME FEATURES OF THE BEHAVIOR OF Rh(III) COMPLEX COMPOUNDS IN SOLUTION, ASSOCIATED WITH THE COMPENSATION EFFECT

The compensation effect ($^{1-4}$) is expressed in the form of the dependence

$$\Delta S^{\neq} = \nu \Delta H^{\neq} + \alpha, \tag{1}$$

where α and ν are constants characteristic of each class of reactions.

Analogous relations have been found for the thermodynamic characteristics of reaction equilibria; the heat and entropy of reactions are related by the equation ($^{4-6}$):

$$\Delta S_0 = \nu \Delta H_0 + \alpha_1. \tag{2}$$

Fulfillment of relation (1) for the kinetic characteristics of reversible reactions proceeding in the forward and reverse directions leads to dependence (2) between the quantities ΔS_0 and ΔH_0, which characterize the reaction equilibrium (^{6}).

In Fig. 1 the kinetic characteristics of the hydrolysis of Rh(III) complex ions are presented in the coordinates $\Delta H^{\neq}$ and $\Delta S^{\neq}$. Despite the small interval of variation of the quantities plotted along the axes, it can nevertheless be said that they are interrelated according to equation (1), with parameters $\nu = 3 \cdot 10^{-3}$, $\alpha = -65$. The "inversion" temperature T_0 corresponding to this value of ν (^{1,3,6}) lies in the range 60-70°. At a temperature equal to T_0, the rate constants of all reactions (independently of the value of $\Delta H^{\neq}$) that obey relation (1) should be close to one another. Indeed, rate constants at temperatures close to T_0, not very strongly differing from one another, have been obtained for the hydrolysis of $\mathrm{Rh(NH_3)_5X}$, where $\mathrm{X = Cl, Br, I, CH_3COO, CF_3COO}$ (^{7,8}). The rate constants of substitution reactions of the type (^{10}): trans-$(\mathrm{Rhen_2Cl_2}) + 2\mathrm{X}$, where en is ethylenediamine, also retain a surprising constancy at 80° ($k = 4 \div 5 \cdot 10^{-5}$ sec^{-1}), despite the fact that such addends as $\mathrm{OH^-}$, $\mathrm{Cl^-}$, I, $\mathrm{NH_3}$, $\mathrm{NO_2^-}$, $\mathrm{S_2O_3^{2-}}$, and thiourea are used, which for the corresponding platinum compounds at 25° possess strongly differing abilities to enter the inner sphere. Cis- and trans-$[\mathrm{Rhen_2Cl_2}]^+$ differ at temperatures close to T_0 in the rate of hydrolysis by no more than a factor of ten (10). Hydrolysis of $[Rh(C_2O_4)_3]^{3-}$ also proceeds at 70° with a rate constant equal to $1.6 \cdot 10^{-4}$ sec^{-1} (9). The closeness of the rate constants seems natural in view of the applicability of relation (1) to these reactions and the closeness of the measurement temperature to the inversion temperature T_0.

Since the equilibrium constant is equal to the ratio of the rate constants of the forward and reverse reactions, then, by virtue of the closeness of the rate constants to one another at temperatures T_0, the values of the equilibrium constants at these temperatures should not be far from 1.

Fig. 1. Dependence of the activation heat $\Delta H^{\neq}$ on the activation entropy $\Delta S^{\neq}$ for reactions of complex ions of Rh(III):
1 $-[Rh(NH_3)_5Cl]^{2+} + H_2O$ (7);
2 $-[Rh(NH_3)_5C(CH_3)_3COO]^{2+} + H_2O$ (8);
3 $-[Rh(NH_3)_5CF_3COO]^{2+} + H_2O$ (8);
4 $-[Rh(NH_3)_5CH_3COO]^{2+} + H_2O$ (8);
5 $-[Rh(NH_3)_5Br]^{2+} + H_2O$ (7);
6 $-[Rh(C_2O_4)_3]^{3-} + H_2O$ (9);
7 $-[RhCl_6]^{3-} + H_2O$ (our data).

We determined the equilibrium constant of the aquation reaction of $RhCl_6^{3-}$ from the equation:

$$RhCl_6^{3-} + H_2O \rightleftarrows RhCl_5H_2O^{2-} + Cl^-. \qquad (3)$$

The constant was determined by the method of shifted equilibrium (11). A solution of K_3RhCl_6 with concentration 10^{-3} mole in 0.1 N $NClO_4$ was titrated with silver nitrate, using a silver electrode as the indicator electrode. The value obtained for the equilibrium constant, $k = 1.1$ ($t = 15°$), is indeed close to unity.

The rate of acidification after dissolution of a weighed portion of K_3RhCl_6 in 0.1 N KNO_3 was also measured over a wide temperature range including the inversion temperature. The measurements were carried out with a glass electrode, with recording of pH values on an EPPV-60 recorder. The recorder scale was calibrated with standard buffer solutions at the temperatures of the kinetic experiments (from 25 to 84°). The rate constants were calculated from pH values in the region of low buffer capacity of the solution, from the initial portions of the kinetic curves. Fig. 2 illustrates the subordination of the temperature dependence of the reaction-rate constant to the Arrhenius equation. The obtained value of the activation heat,

$$\Delta H^{\ddagger} = 26.4 \text{ kcal},$$

and the activation entropy,

Fig. 2. Dependence of the rate constant on temperature for the reaction $[RhCl_6]^{3-} \rightarrow H_2O$

Figure 1: Fig. 2. Dependence of the rate constant on temperature for the reaction $[RhCl_6]^{3-} \rightarrow H_2O$

$$\Delta S^{\ddagger} = +1.0 \text{ entropy units,}$$

confirm relation (1).

Fig. 2. Dependence of the rate constant on temperature for the reaction $[RhCl_6]^{3-} \rightarrow H_2O$.

It is of interest that the rate constant of reaction (3) has, at 70°, the value $1.26 \cdot 10^{-4}$ s^{-1}, which is very close to the values of the constants for other reactions obtained in the works mentioned above for this temperature region.

Let us note that a temperature "not exceeding 50°" is also indicated in Brauer' s handbook ([12]) in the description of the synthesis of isomeric sulfate complexes of rhodium: the "yellow" sulfate changes into the "red" one upon heating above this temperature.

An exact determination of T_0 is hardly possible at present, since there are no kinetic data with a large interval of variation of $\Delta H^{\ddagger}$. We did not attempt to do this; we only wished to draw attention to the possibility of considering kinetic and thermodynamic data from a single point of view, which, apparently, may in some cases prove useful, especially for testing various hypotheses underlying the explanation of the compensation effect ([1,2,5,13]).

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Note: Figure translations are in progress. See original paper for figures.