KINETICS AND EQUILIBRIUM OF COMPLEX FORMATION BETWEEN THE PALLADIUM (II) AQUOION AND AROMATIC AMINES IN AQUEOUS SOLUTION

M. N. Vargaftik, É. D. German,
R. R. Dogonadze, and Academician Ya. K. Syrkin

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We have investigated the kinetics and equilibrium of the complex formation in aqueous solution between the tetraaquopalladium(II) ion and a series of closely structurally related uncharged ligands (aniline derivatives) with the aim of studying the reactivity of palladium (II) complexes in ligand substitution reactions

$$Pd(H_2O)_4^{2+} + H_2NC_6H_4X \rightleftarrows Pd(H_2NC_6H_4X)(H_2O)_3^{2+} + H_2O, \quad (1)$$

where X = p-OCH_3, m-CH_3, p-CH_3, H, m-Br, m-NO_2, and p-NO_2. The ionic strength of the solution was held constant at 2.0 M and the kinetics were investigated over the temperature range from 5 to 35°C.

When solutions of palladium perchlorate ($\sim 10^{-4}$ M) and aniline ($\sim 10^{-2}$ M) in 2 M $HClO_4$ are mixed, it is observed that the optical density of the solution increases exponentially with time and is accompanied by the appearance of a new absorption maximum at 290 mμ. An analysis of the dependence of the equilibrium optical density on the concentration of aniline shows that one molecule of aniline is involved in the complex formation and that the stability constant of the complex is of the order of 10^7 M^{-1}. When concentrated $HClO_4$ is added to a solution in which the equilibrium has been established, the optical density at 290 mμ decreases exponentially with time according to the same law as observed for the forward reaction. This latter fact suggests that the complex formation is reversible. Similar changes in the optical density in the region from 280 to 320 mμ were also observed in the case of the other amines in the given series.

The high values of the stability constants allow one to study the complex formation in highly acidic media where the palladium (II) ion exists solely in the aquoform [1, 2] and the equilibrium ionization of the amines

$$H_2NC_6H_4X + H^+ \rightleftarrows H_3N^+C_6H_4X \quad (2)$$

is strongly displaced to the right hand side with the concentration of the basic form of the amine lying within the limits from 10^{-5} to 10^{-8} for a total concentration of about 10^{-2} M in the solution. Under these conditions reaction (1) has a halftime of 1 to 100 minutes and its rate can be measured using the conventional spectroscopic method.

The kinetic experiments were carried out under zeroth order conditions with respect to the amine since the total concentration of the amine exceeded the concentration of the palladium ions by 20 to 200 times. The value of the observed first order rate constant k_{obs} was independent of the initial concentration of $Pd(H_2O)_4^{2+}$ when the concentration was varied from 10^{-4} to 10^{-3} M, but it increased when the concentration of the amine was raised. The concentration of the basic form of the amine was calculated allowing for the equilibrium in Eq. (2) using the pK_a value of the amine at the given temperature [3] and the acidity functions H_0 for the aqueous solutions of $HClO_4$ [4]:

$$\lg([H_3N^+C_6H_4X] / [H_2NC_6H_4X]) = pK_a - H_0. \quad (3)$$

The linear form of the dependence of k_{obs} on the concentration of the basic form of the amine (Fig. 1) confirms that one molecule of the amine participates in reaction (1) since the dependence of k_{obs} on the concentra-

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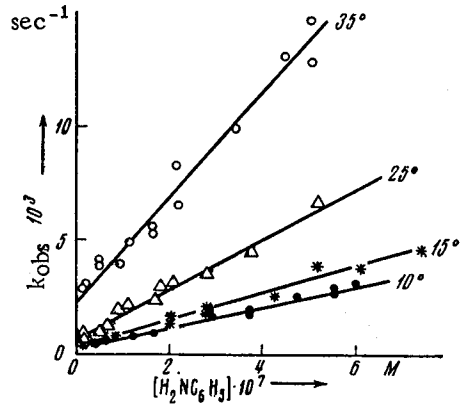

Fig. 1

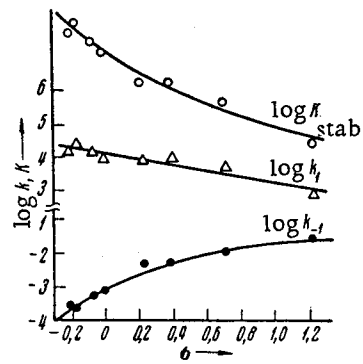

Fig. 2

Fig. 1. Dependence of the observed first order rate constant k_{obs} on the concentration of the basic form of the amine.

Fig. 2. Dependence of the logarithms of the rate constants k_1 and k_{-1} and the equilibrium constant K for reaction (1) on the Hammett σ-constant.

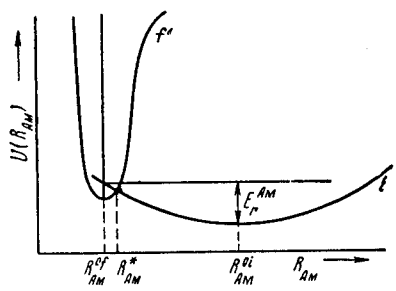

Fig.3

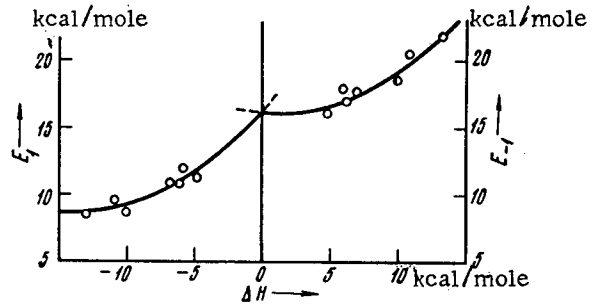

Fig. 4

Fig. 3. A cross-section of the potential energy surface of reaction (1) along the coordinate corresponding to the motion of the entering group (R_{Am}). The difference in energy between the minima of the terms for the initial and final states only corresponds to the heat of reaction along the above-mentioned coordinate. The overall heat of reaction is determined by the position of the minima of the multidimensional terms.

Fig. 4. The dependence of the energy of activation for reaction (1) in the forward and reverse directions on the heat of reaction. The curves are graphical plots of functions (9) and (10) obtained from the experimental data by a least squares treatment.

tion of the basic form of the amine under zeroth order conditions with respect to the amine and H_2O satisfies the equation:

$$k_{obs} = k_1[H_2NC_6H_4X] + k_{-1}, \quad (4)$$

where k_1 is the rate constant for reaction (1) in the forward direction and k_{-1} is the rate constant in the reverse direction. The stability constant of the complex K_{stab} was calculated as the ratio k_1/k_{-1}. The values of K_{stab} obtained by this method coincide with the values found from an analysis of the dependence of the equilibrium optical density on the amine concentration.

The dependence of the forward and reverse rate constants for reaction (1) on temperature obeys the Arrhenius equation for the whole series of amines. The calculated values for the energy of activation and heat of reaction $\Delta H = E_1 - E_{-1}$ are shown in Table 1. The values of k_1 and K_{stab} increase with increasing basicity of the amine or electron donor properties of the substituent in the benzene ring, while the values of k_{-1} decrease along this series. However, the $\rho\sigma$ correlation is only almost linear for k_1 and is nonlinear for k_{-1} and K_{stab} (Fig. 2). The results in Table 1 also show that the reaction series studied is not isentropic.

TABLE 1

Value of X in $H_2NC_6H_4X$	k_1 (25°) M^{-1} sec^{-1}	k_{-1} (25°) sec^{-1}	K_{stab}(25°) M^{-1}	E_1, kcal/mole	E_{-1}, kcal/mole	$\Delta H = E_1 - E_{-1}$, kcal/mole	ΔS^{298}, e.u.
p-OCH_3	$1{,}8\cdot10^4$	$2{,}8\cdot10^{-4}$	$6{,}4\cdot10^7$	11,9	17,8	—5,9	+16
m-CH_3	$1{,}7\cdot10^4$	$4{,}6\cdot10^{-6}$	$3{,}7\cdot10^7$	11,2	16,0	—4,8	+18
p-CH_3	$2{,}3\cdot10^4$	$2{,}1\cdot10^{-4}$	$1{,}1\cdot10^8$	10,8	17,6	—6,8	+14
H	$1{,}1\cdot10^4$	$6{,}8\cdot10^{-4}$	$1{,}6\cdot10^7$	10,8	16,9	—6,1	+12
m-Br	$9{,}8\cdot10^3$	$5{,}0\cdot10^{-3}$	$2{,}0\cdot10^6$	8,5	18,5	—10,0	—5
m-NO_2	$5{,}7\cdot10^3$	$1{,}2\cdot10^{-2}$	$4{,}8\cdot10^5$	9,6	20,4	—10,8	—10
p-NO_2	$9{,}8\cdot10^2$	$2{,}9\cdot10^{-2}$	$3{,}4\cdot10^4$	8,5	21,7	—13,2	—23

At the present time it is difficult to give any clear physical interpretation to the free energies of reactions of the type under consideration. The contemporary quantum mechanical theory of the kinetics of chemical reactions in polar media [5] allows one to give an interpretation to the relationship between the energy of activation and the heat of reaction even in the absence of any detailed information concerning the form of the potential energy surface. The nature of such a relationship depends on the reaction mechanism of (1):

1) Associative type A [6] or S_N2_{lim} [7] with the slow formation of a five coordinate complex followed by a rapid loss of H_2O.

$$Pd(H_2O)_4^{2+} + H_2NC_6H_4X \overset{\text{slow}}{\rightleftarrows} Pd(H_2O_4)\cdot(H_2NC_6H_4X)^{2+} \overset{\text{fast}}{\rightleftarrows} Pd(H_2NC_6H_4X)(H_2O)_3^{2+} + H_2O \qquad (5)$$

2) An associative mechanism of the same type as above but with a rapid first stage and a slow second stage.

3) Synchronous type I_a or S_N2 [7] exchange mechanism.

Both variants of the associative mechanism are described by a single type of kinetic scheme if the reverse reaction is considered in the first case and the forward reaction in the second case. When this is done it follows from the stationary state conditions that the slow stage is only very slightly reversible.

The following features are common to all of the mechanistic variants listed above: 1) all the degrees of freedom of the nuclei participating in the reaction are classical; 2) a charge redistribution occurs during the course of the reaction which leads to a reorganization of the solvent around the reacting particles (during this process the characteristic frequencies of the fluctuations in the polarization remain practically unchanged); 3) the characteristic frequency corresponding to the metal-departing group bond is sharply lowered from 300 to 500 cm^{-1} in the complex to 1 to 10 cm^{-1} in the solvent. The characteristic frequency corresponding to the motion of the entering group is sharply increased.

In the case of the synchronous mechanism, there is a sharp change in the frequencies of both the entering and departing groups in the transition state. During this process the bond between the metal and the departing group is only slightly strained and the entering group is located at a small distance from the metal which is almost coincident with its final distance along this coordinate (Fig. 3). The contribution to the energy of activation of the forward reaction due to the departing group is zero while the contribution from the entering group is E_r^{Am}. Analogously, the contribution to the energy of activation for the reverse reaction from the motion of the amine is equal to zero but a contribution $E_r^{H_2O}$ appears, due to the motion of the H_2O molecule.

According to quantum theory [8], the energy of activation for the forward reaction in the case of the synchronous mechanism can be expressed in the following manner:

$$E_1 = E_r^{Am} + (E_S + \Delta H - E_r^{Am} + E_r^{H_2O})^2/4E_S, \qquad (6)$$

where E_S is the energy of the reorganization of the solvent. The second term in (6) is the contribution to the energy of activation due to the reorganization of the solvent. The relationship (6) also remains valid in the case where some reorganization of the unsubstituted groups takes place during the course of the reaction, provided that the characteristic frequencies do not undergo a sharp change.

In the case of the two stage mechanism, a sharp change in the frequency takes place during the slow stage for just one of the groups, either the departing or the entering group. The observed energy of activation is equal to the sum of the energies of activation for the slow stage and the heat of the preceding equilibrium. In the first variant of the mechanism, the energy of activation of reaction (1) in the reverse direction can be expressed in the form

$$E_{-1} = \Delta H' + (E_S + \Delta H'' + E_r^{Am})^2/4E_S, \qquad (7)$$

where $\Delta H'$ is the heat of reaction for the combination of H_2O with he aminotriaquopalladium (II) ion and $\Delta H''$ is the heat change accompanying the removal of the amine molecule. In the second variant of the associative mechanism, the activation energy for reaction (1) in the forward direction will be expressed in the following manner:

$$E_1 = \Delta H'' + (E_S + \Delta H' + E_r^{H_2O})^2/4E_S. \quad (8)$$

It can be seen from Eqs. (6), (7), and (8) that the dependence of the activation energy for reaction (1) on the heat of reaction is expressed by the equation of a parabola for all three variants of the reaction mechanism. When the experimental data for the dependence of the activation energy on the heat of reaction (Fig. 4) is submitted to a least squares treatment, it leads to equations of the form

$$E_1 = 8.5 + (0.195\Delta H + 2.75)^2 \text{ kcal/mole}, \quad (9)$$

$$E_{-1} = 16.1 + (0.195\Delta H - 0.181)^2 \text{ kcal/mole}. \quad (10)$$

With the help of the numerical values for the coefficients in Eqs. (9) and (10), the parameters occurring in Eqs. (6), (7), and (8) can be determined. When this is done, it turns out that the stage involving the rapid formation of the five coordinate intermediate complex must be endothermic for both variants of the associative mechanism. For the first variant [Eq. (7)] $\Delta H' = +8.5$ and for the second variant [Eq (8)] $\Delta H'' = +16.1$ kcal/mole. It follows from this that the activation energy of the slow stage lies within the limits from 0 to 3.4 kcal/mole (first variant) or 0 to 5.6 kcal/mole (second variant) and must be considerably lower than the activation energy of the proposed fast stage (8.5 or 16.1 kcal/mole, respectively). Furthermore, one of the parameters appearing in Eq. (7) or (8), E_S, E_r^{Am}, or $E_r^{H_2O}$ must be negative, which is physically absurd.

At the same time, Eq. (6) agrees with Eq. (9) when the physically reasonable values $E_s = +6.6$, $E_r^{Am} = +8.5$, and $E_r^{H_2O} = +16.1$ kcal/mole are taken for these parameters. Hence from the point of view of the quantum theory of chemical kinetics in polar media [5], the synchronous exchange mechanism of type I_a or S_N2 is to be considered as the only mechanism which agrees with the experimental results.

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