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Coordination of Aza Heterocycles with Macroheterocyclic Metal Complexes in Amphiprotic Media: III.[1] Kinetics and Mechanism of Inner-Sphere Ligand Exchange in (Tetraphenylporphyrinato)chromium(III)

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Abstract — Inner-sphere replacement of alcohols by imidazole and its derivatives in the complex (acetato)-(tetraphenylporphyrinato)chromium(III) was studied by electronic absorption spectroscopy. The rate constants and activation parameters of the process were calculated. The entering ligand structure was shown to affect the reaction rate, while the alcohol nature (departing ligand) does not influence the kinetic parameters of the process to an appreciable extent. Regression analysis revealed participation of imidazole and ethanol in the rate-determining stages. The kinetic equation for the inner-sphere axial substitution implies interaction of a free alcohol molecule with that coordinated to chromium, followed by replacement of the associate by the heteroring. Mathematical processing of the kinetic data in terms of the proposed solvolytic association–dissociation mechanism gave the rate constants for particular stages of the process and showed an extremal relation between the rate constant and composition of the solvent.
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Using electronic absorption spectroscopy and ^{1}H NMR we previously showed [1, 2] that coordination of imidazole and its methyl-substituted derivatives to (acetato)(tetraphenylporphyrinato)chromium(III) in alcohols involves successive replacement of two solvent molecules in the sixth coordination site of the complex. The kinetic and activation parameters of the inner-sphere replacement of alcohols [1] indicated S_N2 nucleophilic substitution mechanism of the process and an appreciable effect of the heterocycle structure on the transition state.

Therefore, the next step of our study was aimed at elucidating the kinetics of inner-sphere replacement of alcohols coordinated to (acetato)(tetraphenylporphyrinato)chromium(III) by imidazole (Im) and its derivatives, 1-methylimidazole (1-MeIm), 2-methylimidazole (2-MeIm), and 4-methylimidazole (4-MeIm).

$$(AcO)CrTPP(ROH) + Im \longrightarrow (AcO)CrTPP(Im) + ROH.$$

Here, Im can denote both the outer-sphere ligand and heterocycle molecule in the bulk solution. The reactions were carried out in methanol, ethanol, propan-1-ol, propan-2-ol, and butan-1-ol. The reaction course was monitored by spectrophotometry using excess imidazole and its methyl-substituted derivatives so that to meet the kinetic conditions for irreversible pseudo-first-order reactions.

Table 1 contains the apparent rate constants k_{ap} for the reactions of imidazoles with (AcO)CrTPP···ROH, the true rate constants k_v calculated by the formula $k_v = k_{ap}$/[heterocycle], and activation parameters of the process, calculated from the temperature dependences of $\ln k_{ap}$ (some of these are shown in Fig. 1). Table 2 contains analogous data for the replacement of alcohols by imidazole. It should be noted that inner-sphere substitution of alcohols by heterocycle occurs at a much lower rate than the outer-sphere exchange. It is seen that the rate constants k_{v2} (Tables 1, 2) are smaller than k_{v1} by 2 to 3 orders of magnitude (on the average) [1].

Analysis of the data in Table 1 indicates a weak effect of the departing ligand structure on the kinetic parameters of the replacement process; an exception is the reaction with 2-MeIm, for which k_{v2} is lower by

[1] For communication II, see [1].

Table 1. Rate constants and activation parameters of the inner-sphere replacement of ethanol by aza heterocycles

Heterocycle	k_{ap}, s^{-1} (k_v, $l\,mol^{-1}\,s^{-1}$)					E_a, kJ mol^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J $mol^{-1}\,K^{-1}$
	293 K	298 K	303 K	308 K	313 K				
Im	0.00003 (0.003)	0.000056 (0.006)	0.000196 (0.02)	0.000346 (0.035)	0.00057 (0.058)	117.4	85.7	114.9	97.7
1-MeIm	0.000044 (0.006)	0.000078 (0.01)	0.00012 (0.163)	0.000213 (0.028)	0.000355 (0.047)	79.3	84.3	76.8	–25.2
2-MeIm		0.000025 (0.00053)	0.000044 (0.00096)	0.000083 (0.0018)	0.000185 (0.004)	67.8	80.3	65.3	–50.2
4-MeIm	0.000036 (0.003)	0.000068 (0.006)	0.00014 (0.012)	0.000309 (0.266)	0.000471 (0.406)	101.2	85.7	98.7	43.7

Table 2. Rate constants and activation parameters of the inner-sphere replacement of alcohols by aza heterocycles

Solvent	k_{ap}, s^{-1} (k_v, $l\,mol^{-1}\,s^{-1}$)					E_a, kJ mol^{-1}	$\Delta G^{\neq}$, kJ mol^{-1}	$\Delta H^{\neq}$, kJ mol^{-1}	$\Delta S^{\neq}$, J $mol^{-1}\,K^{-1}$
	293 K	298 K	303 K	308 K	313 K				
CH_3OH	–	0.000123 (0.015)	0.000219 (0.027)	0.000421 (0.052)	0.000741 (0.091)	93.6	83.3	91.2	25.3
C_2H_5OH	0.00003 (0.003)	0.000056 (0.006)	0.000196 (0.02)	0.000346 (0.035)	0.00057 (0.058)	117.4	85.7	114.9	97.7
1-C_3H_7OH	0.000031 (0.003)	0.00005 (0.004)	0.000072 (0.006)	0.000271 (0.023)	0.000314 (0.027)	96.5	86.4	91.2	15.8
2-C_3H_7OH	0.000026 (0.004)	0.000076 (0.013)	0.000253 (0.043)	0.00022 (0.038)	0.000952 (0.163)	126.5	83.7	124.0	135.3
1-C_4H_9OH	0.000017 (0.003)	0.000035 (0.005)	0.000067 (0.010)	–	0.000181 (0.027)	95.8	86.0	93.4	24.8

an order of magnitude that the corresponding rate constants for the other heterocycles. The reaction rate strongly depends on the heterocycle concentration. In the first reaction step, 2-MeIm was also characterized by the lowest k_{v1} values, which may be due to spatial proximity of the substituent and reaction center and considerable steric hindrances. However, the rate of the reaction with the other heterocycles changed in parallel with their basicity, and no such relation was observed in the second step (Table 1). The low reactivity of 2-MeIm may be rationalized in terms of steric hindrances in the reaction between the metal complex and the heterocycle.

The kinetic data given in Table 2 show a very slight dependence of the rate and activation parameters of the inner-sphere replacement upon alcohol nature. The second-order rate constant k_{v2} at 298 K changes from 0.004 to 0.015 $l\,mol^{-1}\,s^{-1}$, and we have not succeeded in finding any reliable correlation between $\ln k_{v2}$, on the one hand, and solvent polarity (Kirkwood factor) and electron-donor (donor number *DN*) or electron-acceptor power (acceptor number *AN* and Reichardt electrophilicity parameters E_T) of the departing ligand, on the other.

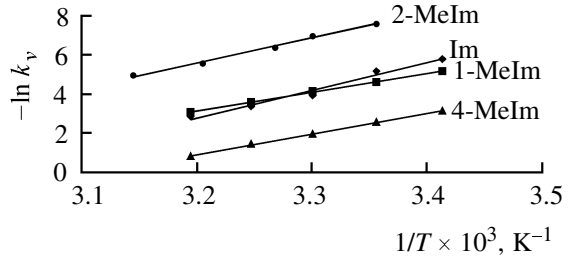
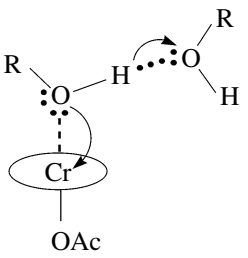


Fig. 1. Plots of the logarithm of the rate constant ($\ln k_v$) for the replacement of ethanol by imidazole ($R^2 = 0.976$), 1-methylimidazole ($R^2 = 0.999$), 2-methylimidazole ($R^2 = 0.991$), and 4-methylimidazole ($R^2 = 0.997$) versus reciprocal temperature. Linear correlation coefficients are given in parentheses.

The observed fairly weak and ambiguous effects of the leaving and entering ligands on the kinetics of inner-sphere substitution did not allow us to draw a definite conclusion on the reaction mechanism. Comparison of our results with the available data on the reactivity of chromiun(III) porphyrin complexes showed that weak-field ligands (containing oxygen, sulfur, or phosphorus) in weakly solvating media (such as toluene) are replaced at a very high rate [3, 4] which exceeds k_{ap} values obtained at comparable imidazole concentrations by 3–5 orders of magnitude. The high rates of substitution led the authors of [3, 4] to presume a strong labilizing effect arising from steric destabilization of the axial ligand at the side of the macroring. Typical features of the dissociative substitution mechanism (S_N1) were also observed: weak effect of the entering ligand and strong effect of the departing ligand. The labilizing effect was also revealed in the replacement of water in aqueous medium [5]. It was rationalized from the viewpoint of *trans* effect of the active hydroxo ligand in the fifth coordination site of the complex. The substitution of water in bis-aqua complexes is slow, and its rate is comparable with our data. A probable reason is stabilization of the aqua ligand in the first coordination sphere via hydrogen bonding with an outer-sphere molecule and electron density redistribution from the latter to chromium. However, no clear-cut conclusion can be drawn from comparison of the kinetic data, for replacement processes in aqueous medium involve charged complexes, and they may be accompanied by ionization of imidazole and other side reactions that are not typical of less polar and less solvating alcohols. Taking the above stated into account, it should be noted that our kinetic data for the inner-sphere substitution do not conform to dissotiative S_N1 mechanism. On the other hand, we revealed no appreciable effect of the entering ligand, which is typical of formation of a seven-coordinate complex (transition state like "octahedral wedge") inherent in the $S_N2_{(lim)}$ mechanism [6].

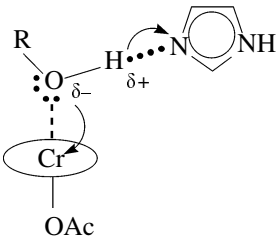
Presumably, the stability of macrocyclic chromium(III) complexes with axial hydroxy-containing ligands (water, alcohols) is determined by hydrogen bonding with electron-donor molecules (water, alcohols, aza heterocycles, etc.) in the second coordination sphere, which promotes electron density transfer from the outer-sphere ligand to the chromium atom (Scheme 1).

Scheme 1.



Obviously, the strongest effect should be observed for the outer-sphere complex with strongly electron-donor imidazole (Scheme 2).

Scheme 2.



The above considerations prompted us to perform additional kinetic experiments with a view to elucidate the mechanism of axial inner-sphere substitution. For this purpose, we examined the kinetics of the process in mixed solvents, namely, in chloroform–ethanol and chloroform–methanol. Figure 2 shows the dependences of the apparent pseudo-first-order rate constants upon composition of the binary solvent; these dependences are clearly nonmonotonic. Taking into account unusual shape of the curves, specific attention was given to the reproducibility of the obtained data. It was firmly established that the absolute maximum in the region of low alcohol concentrations and the local minima at c_{EtOH} = 0.4–0.5 and c_{MeOH} = 0.25–0.3 M (Fig. 2) are retained upon variation of the alcohol nature, imidazole concentration, and temperature; therefore, these dependences cannot be accidental.

The simplest rationalization of these data may be nonmonotonic character of variation of macroproperties of the medium, in particular the effect of solvent polarity on the reaction rate. Therefore, we plotted dependences of k_{ap} upon the Kirkwood factor for methanol–chloroform and ethanol–chloroform mixtures. The shape of the obtained curves was fully identical to that of the concentration dependence of k_{ap}, indicating that our assumption is invalid.

Another reason for the anomalous character of the $k_{ap2} = f(c_{AlkOH})$ curves may be effect of the composition of binary solvent on association and solvation of both the alcohol and imidazole (taking into account their amphoteric properties). The positions of the local extrema on the kinetic curves in the concentration ranges 0.4–0.5 M for ethanol and 0.25–0.3 M for methanol almost coincide with the azeotrope compo-

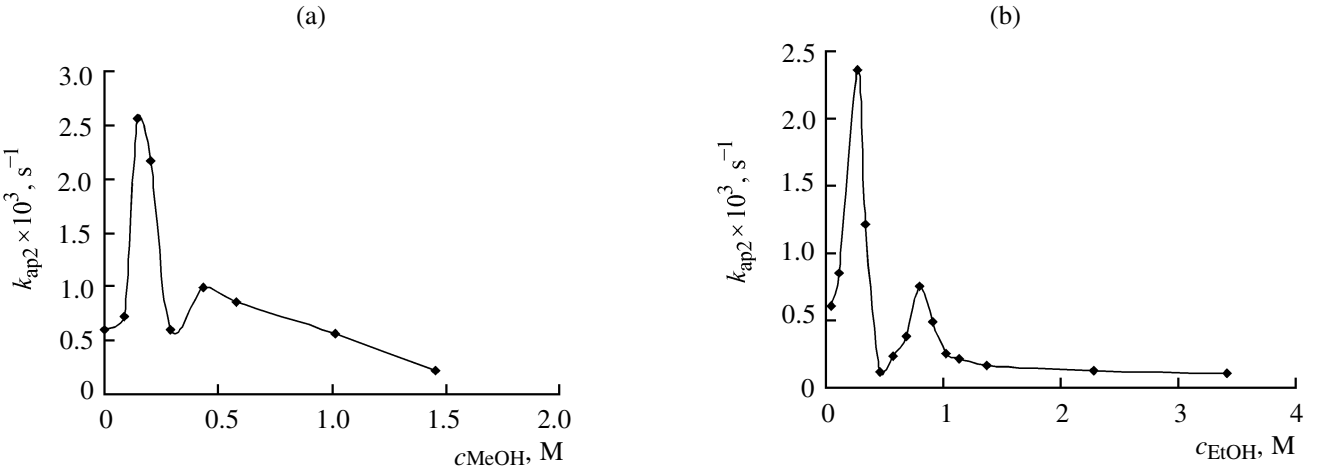


Fig. 2. Plots of k_{ap2} versus the composition of binary solvent: (a) chloroform–methanol and (b) chloroform–ethanol.

sitions of ethanol–chloroform and methanol–chloroform binary mixtures [7]. It is known that, from the viewpoint of thermodynamics, azeotropes behave like individual substances, regardless of the number of components [8]. In fact, the values of k_{ap2} in the region of azeotrope composition are close to k_{ap2} values for individual alcohols.

Thus, the local minima in the kinetic curves may be interpreted as corresponding to azeotrope composition of the binary solvent, while the maxima on the $k_{ap2} = f(c_{AlkOH})$ curves cannot be explained in such a way. To elucidate main factors affecting the kinetic parameters of the process, we have resorted to complete factorial and orthogonal central compositional planning techniques [9, 10]. Experiments were performed in ethanol–chloroform binary solvent with compositions corresponding to the ascending and descending branches of the kinetic curve $k_{ap2} = f(c_{AlkOH})$. As independent variables x_1 and x_2 we selected the concentration of ethanol and imidazole, respectively. For the ascending and descending branches we obtained Eqs. (1) and (2), respectively:

$$Y = 0.0004555 + 0.004065x_1 + 2.09694x_2, \quad (1)$$

$$Y = 0.001848 - 0.003272x_1 + 4.36735x_2 + 0.001085x_1^2. \quad (2)$$

Analysis of these regressions shows that increase of the imidazole concentration favors inner-sphere ligand replacement (the corresponding coefficients in each equation are positive). The effect of the alcohol changes with its concentration: it initially favors the process [positive coefficient at x_1 in Eq. (1)] and then inhibits the reaction [negative coefficient at x_1 in Eq. (2)]. Joint solution of the equations describing the rise and the drop of k_{ap2} gives $x_1 = 0.26$ M; this value coincides with the ethanol concentration at the maximum on the experimental curve $k_{ap2} = f(c_{EtOH})$.

Regression analysis unambiguously established participation of ethanol in the rate-determining stages. However, the difficulty is that the alcohol is a departing ligand and solvent simultaneously. Taking into account amphiprotic character and considerable solvating power of ethanol, strong effect of the composition of binary solvent on association of the alcohol and solvation of imidazole should be expected, as it was shown [11, 12]. Using the data of [13], we have plotted the concentrations of monomeric alcohols and the average degrees of association of ethanol and methanol against the composition of chloroform–alcohol binary mixture (Fig. 3). Figure 4 shows the dependences of the concentrations of imidazole associates and solvated forms on the composition of ethanol–chloroform binary mixture, which were plotted on the basis of the stability constants given in [12, 14] (the initial imidazole concentration, 1.96×10^{-4} M, corresponded to the experimental conditions). Analysis of the above data led us to conclude that the role of alcohol in the axial ligand exchange is related to (1) the presence of its monomeric molecules in solution and (2) binding of free imidazole into H complex possessing lower reactivity.

In fact, monotonic increase in the alcohol concentration is accompanied by increase in the degree of its association and in the number of associates (Fig. 3), which cannot explain the nonmonotonic character of the $k_{ap2} = f(c_{EtOH})$ dependence. The concentration of monomeric alcohol sharply increases with rise in the overall alcohol concentration, and it reaches is almost maximal value at $c_{EtOH} = 0.6$ M and $c_{MeOH} = 0.3$ M (Fig. 3), i.e., within the concentration range of the absolute maximum on the kinetic curve (Fig. 2). The subsequent drop of k_{ap2} is likely to result from decrease in the concentration of free monomeric imidazole (Fig. 4) acting as entering ligand.

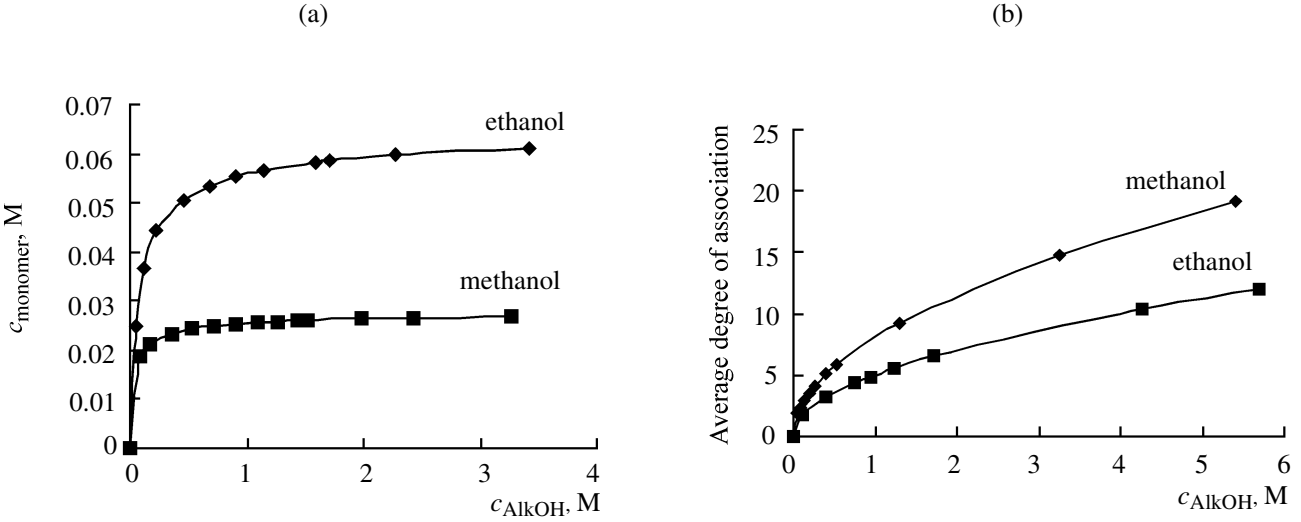
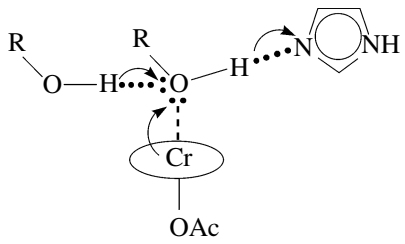


Fig. 3. Dependences of the concentration of (a) monomeric ethanol and methanol and (b) average degree of association upon alcohol concentration in chloroform.

The proposed mechanism of activation by the alcohol of its replacement by heterocycle seems to be fairly unusual; therefore, it requires special structural (stereochemical) and kinetic substantiation. As shown above, the high stability of complexes with hydroxy compounds is the result of formation of outer-sphere H complex with electron donor and electron density transfer from the latter to the central metal ion (Scheme 1). Outer-sphere replacement of alcohol molecule by a stronger electron donor (imidazole) should favor strengthening of the Cr–ROH bond (Scheme 2). Taking into account the d_{z^2} symmetry [15] of the metal orbital responsible for axial σ-coordination with the unshared electron pair on the oxygen atom having tetrahedral configuration, the second *n*-electron pair may be considered to be free; therefore, it may be involved in donor–acceptor interactions, in particular, in hydrogen bonding with another alcohol molecule (Scheme 3). It is clear that proton donor should be free monomeric alcohol molecule, for specific association prevents alcohol molecules from participating in such interactions. Outer-sphere hydrogen bonding should reduce the overall electron density on the oxygen atom in the coordinated alcohol molecule, and hence the dative Cr–O bond in the sixth coordination site of the octahedral complex should become weaker.

Scheme 3.



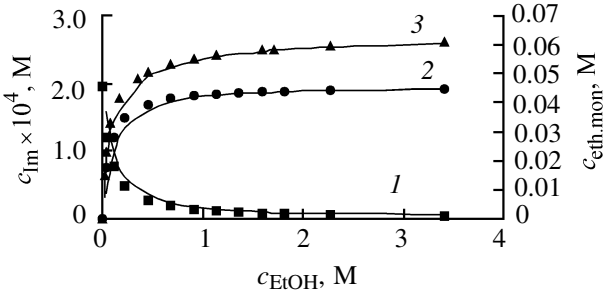


Fig. 4. Dependences of the concentration of (*1*) monomeric imidazole, (*2*) imidazole–ethanol complex, and (*3*) monomeric ethanol upon ethanol concentration in binary mixture ethanol–chloroform. Overall imidazole concentration $c_{Im} = 1.96 \times 10^{-4}$ M.

The proposed mechanism is analogous to some extent to the mechanism presumed previously by Adamson [16] and Jones [17] for the replacement of chloride ion in the complex $Co^{III}(NH_3)_5Cl$ by water molecule, which is activated via H-complex formation by the departing ligand and the remaining ammonia molecule with the second water molecule. Such exchange mechanism was designated in [16] as S_N2FS (frontside), while in [17] it was referred to as solvent-assisted dissociation. However, the principal difference from the mechanism discussed in the present work is that the hydration process is activated by water, i.e., by the entering ligand, while coordination of imidazole (Scheme 3) is activated by the alcohol, i.e., by the departing ligand.

Thus, the general scheme of the examined inner-sphere ligand exchange may be represented as follows:

$$\begin{array}{c}(AcO)CrTPP(ROH) + ROH\\ \mathbf{A}\\ \overset{k_1}{\underset{k_2}{\rightleftarrows}}\ (AcO)CrTPP(ROH)_2 + Im\\ \mathbf{B}\\ \xrightarrow{k_3}\ (AcO)CrTPP(Im) + (ROH)_2.\\ \mathbf{C}\end{array} \qquad (3)$$

For the sake of simplicity, imidazole molecule giving rise to outer-sphere complex is not shown, assuming that it does not play an active role in the process. Actually, participation of imidazole in reaction (3) implies the necessity of preliminary dissociation of the outer-sphere H complex.

To deduce the kinetic equation, let us assume steady state for reactive intermediate **B**. This assumption is quite reasonable, taking into account low stability of intermediate **B** because of steric repulsion between the second alcohol molecule and the macrocyclic ligand and weak electron-donor power of the oxygen atom coordinated to chromium. Then, the rate of formation of intermediate **B** should be equal to the rate of its consumption:

$$k_1[\mathbf{A}][ROH] = k_2[\mathbf{B}] + k_3[\mathbf{B}][Im], \qquad (4)$$

$$[B] = \frac{k_1[\mathbf{A}][ROH]}{k_2 + k_3[Im]}, \qquad (5)$$

$$\frac{d[\mathbf{C}]}{d\tau} = k_{ap}[\mathbf{A}] = \frac{k_1k_3[\mathbf{A}][ROH][Im]}{k_2 + k_3[Im]}, \qquad (6)$$

$$k_{ap} = \frac{k_1k_3[ROH][Im]}{k_2 + k_3[Im]}. \qquad (7)$$

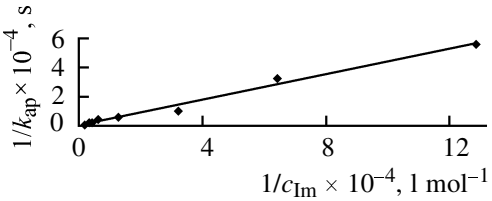


Fig. 5. Plot of $1/k_{ap}$ versus reciprocal concentration of monomeric imidazole for the inner-sphere replacement of alcohol by imidazole; $c_{(AcO)CrTPP} = 1.87 \times 10^{-5}$ M.

After some transformations we obtain Eq. (8):

$$\frac{1}{k_{ap}} = \frac{1}{k_1[ROH]} + \frac{k_2}{k_1k_3[ROH]}\frac{1}{[Im]}. \qquad (8)$$

If the proposed kinetic scheme is valid, the dependence $1/k_{ap} = f(1/[Im])$ at [ROH] = const should be linear. Therefore, we measured experimentally the apparent pseud-ofirst-order rate constants for the inner-sphere replacement of ethanol by imidazole at different concentrations of the latter in ethanol at 298 K. The k_{ap} values and the stability constants of imidazole associates and H complexes Im–EtOH were used to plot the dependence of $1/k_{ap}$ upon reciprocal concentration of free monomeric imidazole (Fig. 5).

The dependence shown in Fig. 5 is satisfactorily approximated by a straight line (correlation coefficient $R^2 = 0.986$); the rate constant k_1 was estimated at 0.062 l mol^{-1} s^{-1}, and the ratio k_2/k_3, at 0.00018. These results allowed us to simulate concentration dependence of the apparent rate constant of the inner-sphere ligand exchange. The theoretical curve shown in Fig. 6b has a maximum whose position satisfactorily corresponds to the experimental dependence (Fig. 6a). Perfect coincidence of the experimental and theoretical curves is not observed for quite clear

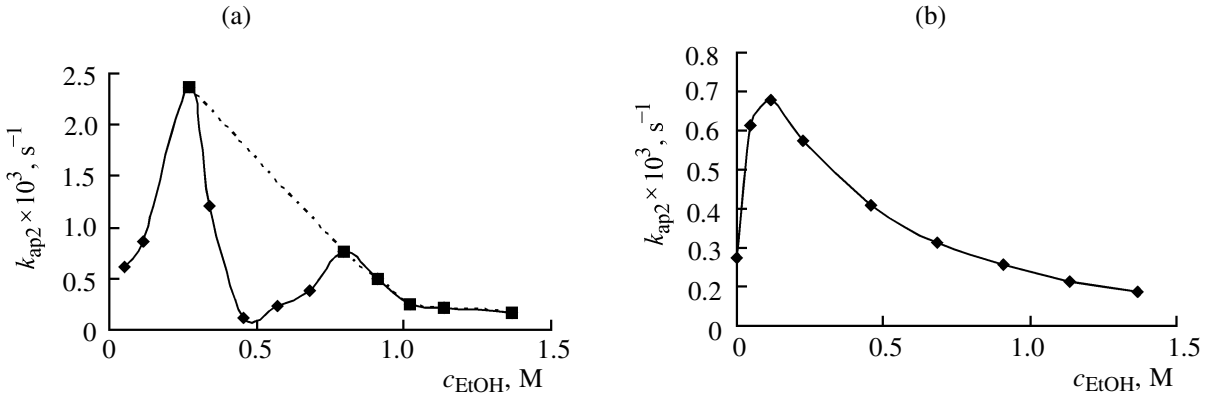


Fig. 6. Plots of the apparent rate constant for the inner-sphere replacement of ethanol by imidazole versus concentration of ethanol in binary mixture ethanol–chloroform: (a) experimental curve (the experimental curve with no account taken of the azeotrope region is shown with a dotted line) and (b) theoretical curve.

reasons. First, it is impossible to simulate conditions of azeotrope composition ensuring appearance of a local extremum. Second, the kinetic curve for binary solvent with variable composition was simulated using the rate constants k_1 and k_2/k_3 calculated for the replacement of ethanol at the axial position of (acetato)(tetraphenylporphyrinato)chromium(III) by aza heterocycles in an individual solvent.

On the other hand, satisfactory agreement between the experimental (Fig. 6a) and theoretical kinetic curves (Fig. 6b) confirms our previous assumptions on solvolytic association–dissociation mechanism of the inner-sphere replacement of alcohols. The principal specificity of the proposed mechanism is activation of axial ligand exchange via interaction of the departing ligand with the second alcohol molecule.

EXPERIMENTAL

The complex (AcO)Cr(III)TPP was kindly provided by Prof. A.S. Semeikin. The complex was additionally purified by chromatography on aluminum oxide (activity grade IV) using chloroform–methanol as eluent. The electronic absorption spectrum of the complex in chloroform was consistent with published data for Cr(III) complexes [18–20]. The solvents were purified according to the known procedures [21, 22]. Imidazole, 1-methylimidazole, 2-methylimidazole, and 4-methylimidazole (Merck–Schuchardt) contained no less than 99% of the main substance and were used without additional purification.

The electronic absorption spectra were recorded on a Perkin–Elmer UV/VIS Lambda 20 spectrophotometer. All measurements were performed using standard quartz cells (cell path length 0.5 and 1 cm).

The rate constants were calculated using a program including two procedures; the procedures are based on measurement of optical density in the maximally possible number of points in a series of spectra recorded in a digital mode. The calculations were performed using the generalized nonlinear least-squares procedure involving the deformable polygon technique. In each point, deviations of all calculated parameters were determined by linearization. Both nonuniformity in the optical density measurements and correlation between the errors in the neighboring points of the spectrum were taken into account, so that not only optimal estimates of parameters but also reliable estimates of their deviations were obtained. The final rate constants were calculated as weighted average values by all points included in the calculation. Points in which the deviation considerably exceeded the calculated parameter were excluded. The error in the determination of the rate constants did not exceed 5%. The activation energies were determined from the graphical dependence of $\ln k_{ap}$ upon $1/T$. The enthalpies, Gibbs energies, and entropies were calculated by the known equations [23]. The error in the determination of the activation energies, and of the enthalpies, Gibbs energies, and entropies did not exceed 7%.

ACKNOWLEDGMENTS

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