

Kinetics & Mechanism of Substitution of Dibutyldichloro-(1,10-phenanthroline)tin(IV) by Chloride Ion

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The kinetics of nucleophilic substitution of dibutyldichloro(1,10-phenanthroline)tin(IV) by chloride ion in nitrobenzene follows first order kinetics. A millimolar solution of the complex in nitrobenzene shows increase in conductance with time due to solvation of the molecule. The conductance is enhanced in the presence of nucleophiles namely, thionyl chloride, acetyl chloride and benzoyl chloride suggesting the substitution of 1,10-phenanthroline by chloride ion. The rate constants for solvation, K_S and for substitution K_1, K_2 have been calculated. The results show that $K_1, K_2 > K_S$ and the reaction follows an S_N1 mechanism.

The conductometric investigations on the kinetics of nucleophilic substitution reactions in octahedral complexes of transition metal ions¹⁻³ and those of group (IV) metal halide⁴⁻⁷ have shown increase in conductance with time. The conductance attained a constant value equal to that a uni-univalent electrolyte.

In continuation of our earlier work⁸ we report herein the kinetics of solvation and substitution of dibutyldichloro(1,10-phenanthroline)tin(IV) by chloride ion liberated by nucleophilic reagents such as thionyl chloride, acetyl chloride and benzoyl chloride. A probable mechanism for substitution has been proposed.

Materials and Methods

Millimolar solution of dibutyldichloro-(1,10-phenanthroline)tin(IV) was prepared in nitrobenzene and its conductance measured as a function of time. From the slope of the linear portion of molar conductance versus time curve (Fig. 1) the specific rate constant for solvation, K_S , was calculated. The solutions of the nucleophile (thionyl chloride, acetyl chloride or benzoyl chloride) and the complex were

mixed separately in three different molar ratios. The conductance of each mixture was measured immediately and at five-minute interval for a period of 1 hr, and after 24 hr to get the value of Λ_∞ .

Results and Discussion

The molar conductance, Λ_M versus time curve for substitution (Fig. 2) was similar to that obtained for solvation (Fig. 1). The value of K_S obtained from the plot in Fig. 1 was found to be $1 \times 10^{-3} \text{ s}^{-1}$.

The plots of $\log[\Lambda_\infty/\Lambda_\infty - \Lambda_M]$ against time consisted of two linear portions (Fig. 3) for different molar ratios of the reactants indicating that both the reactions, i.e. solvation and substitution follow first order kinetics. The specific rate constants, K_1 and K_2 were calculated from the slopes of the first and second linear portions of the curves, respectively using the method of two mutually intersecting lines^{7,8} (Table I). The kinetics of solvation as well as substitution reaction of dibutyldichloro(1,10-phenanthroline)tin(IV) were

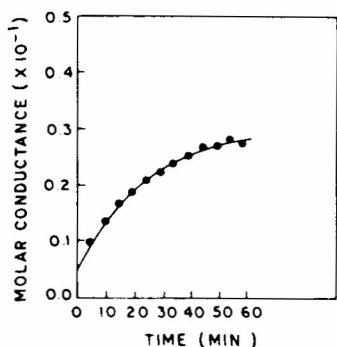


Fig. 1—Molar conductance versus time curve for dibutyldichloro-(1,10-phenanthroline)tin(IV) in nitrobenzene

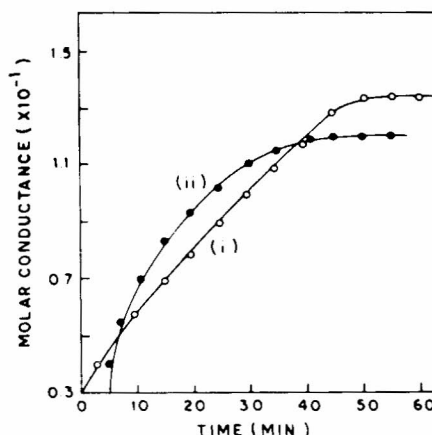


Fig. 2—Molar conductance versus time curves for dibutyldichloro(1,10-phenanthroline)tin(IV) in the presence of (i) CH_3COCl and (ii) $\text{C}_6\text{H}_5\text{COCl}$ in nitrobenzene

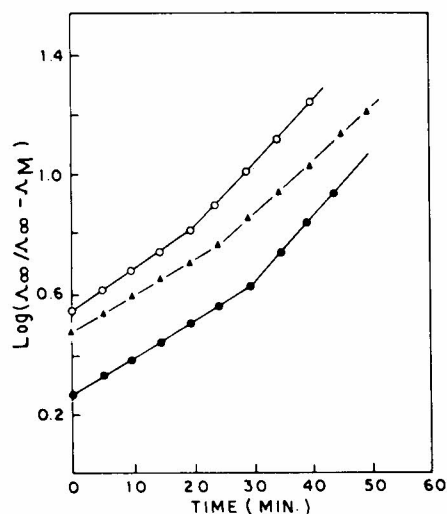
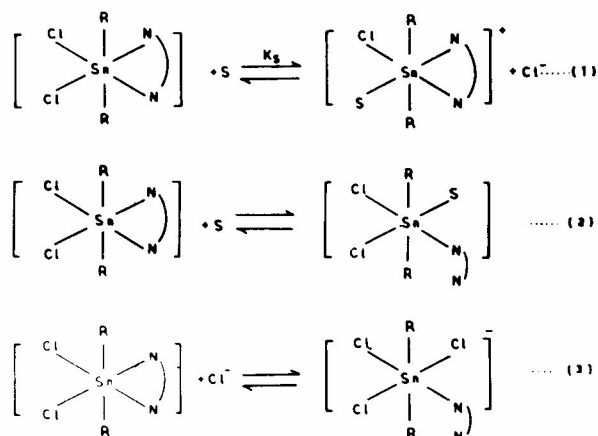


Fig. 3—First order plots for substitution of chloride ion generated from SOCl_2 in dibutyldichloro(1,10-phenanthroline)tin(IV) at different molar ratios in nitrobenzene

investigated in nitrobenzene due to the following reasons: (i) solubility of the complex; and (ii) non self-ionizing character of the solvent⁹.

The conductance of millimolar solution of the complex in nitrobenzene increases with time. The calculated values of the first order rate constant, K_S of solvation show that K_S depends upon initial [complex]. In order to explain these results the reactions (1-3) leading to the formation of an ion-pair involving nitrobenzene are assumed to take place in solution. During solvation the rate of increase in molar conductance in the initial stage is very slow which may be explained on the basis of the reactions (1) and (3) which generate ionic species.



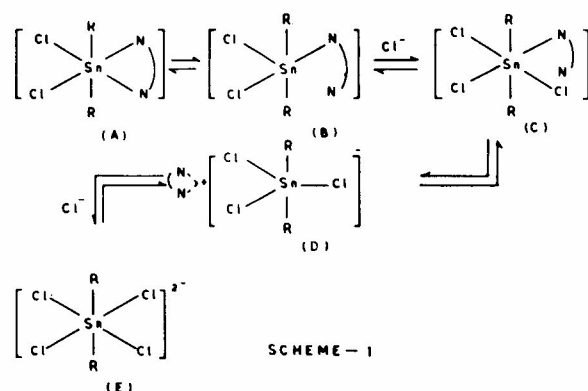
The replacement of the stronger nucleophile, the chloride ion and 1,10-phenanthroline by the solvent (S) is due to the mass effect. The addition of 1,10-phenanthroline, however, affects reaction (3) so that

Table 1—Rate Constants for Substitution of Base Molecule by Chloride Ion in Dibutyldichloro-(1,10-phenanthroline)tin(IV) by Different Nucleophilic Reagents

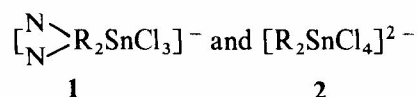
Nucleophilic reagent	Complex/reagent ratio	$K_1 \times 10^{-2}$ (s^{-1})	$K_2 \times 10^{-2}$ (s^{-1})
SOCl_2	1:1	1.4	2.3
	1:2	1.4	2.3
	1:Excess	1.4	2.3
$\text{C}_6\text{H}_5\text{COCl}$	1:1	1.1	1.6
	1:2	1.1	1.6
	1:Excess	1.1	1.6
CH_3COCl	1:1	1.0	1.2
	1:2	1.0	1.2
	1:Excess	1.0	1.2

the consumption of chloride ion is suppressed, as a result of which the equilibrium is shifted to the left in reaction (1), consequently less ionic species are produced which decrease the rate of solvation. As reactions (1) and (3) are fast, therefore, reaction (2) becomes the rate-determining step.

The substitution of 1,10-phenanthroline by chloride ions generated by nucleophilic reagents may follow two paths¹⁰: (a) first order dissociation of 1,10-phenanthroline from the complex followed by rapid addition of chloride ion; and (b) second order reaction with direct attack of chloride ion followed by rapid addition of another chloride ion. However, in the present case it has been found to follow first order (S_N1) reaction for which we propose a mechanism shown in Scheme 1.



The rate of increase in conductance during substitution indicates that the chloride ion is a stronger nucleophile than 1,10-phenanthroline and nitrobenzene. The breaking of one of the two bonds in the complex by chloride ion, results in the formation of



species (1) and (2) as final products and is accompanied by an increase in molar conductance of the solution as a function of time, the conductance attaining a maximum value after 1 hr. The pathway shown, however, involves a trigonal bipyramidal intermediate¹¹⁻¹³. The dissociation of species (1) in step-C (Scheme 1) seems to be faster than the corresponding breaking of one of the two bonds in step-B because of the negative charge on the former which assists the breaking of tin-ligand bond. However, equilibrium is attained after 1 hr. The first order plots consist of two intersecting linear portions (Fig. 3) suggesting that there are two different rate-determining steps, the first step corresponding to the reaction (B), and second to reaction (D).

The results show that the rate of substitution is faster than the rate of solvation. The reaction follows an S_N1 path and the nucleophilic reagents may be arranged in the decreasing order of their rate constants K_1 and K_2 as follows: $\text{SOCl}_2 > \text{C}_6\text{H}_5\text{COCl} > \text{CH}_3\text{COCl}$.

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