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Kinetics & Mechanism of Substitution of Pyrrolidine in Dibutyldichloro-bis(pyrrolidine)tin (IV) by Chloride Ion

K S SIDDIQI*, R I KURESHY, M JARIA & S A A ZAIDI
Department of Chemistry, Aligarh Muslim University,
Aligarh 202 001

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A millimolar solution of dibutyldichloro-bis(pyrrolidine)tin (IV) in nitrobenzene shows an increase in molar conductance with time indicating the solvation of the complex. This increase in conductance is further enhanced in the presence of nucleophiles, namely C_6H_5COCl, $SOCl_2$ and CH_3COCl suggesting the substitution of pyrrolidine by chloride ions. The rate constants for solvation, k_s and for substitution, k_1 and k_2 show that solvation is a slower process as compared with substitution which follows an S_N1 pathway.

Substantial work on nucleophilic substitution reaction in octahedral complexes of transition metal ions[1-3] and those of group (IV) metal halides[4,5] has been done while such studies on organotin compounds are scarce. However, the kinetics of substitution in $[SnCl_4(Py_2)]$, $[Bu_3SnCl(Py)]$ and $[Et_3SnCl(Py)]$ have been studied conductometrically[6-8]. It is observed that in these systems the molar conductances increase with time and attain a value equal to that of an uni-univalent electrolyte.

Presently the kinetics of solvation of the complex $R_2SnCl_2L_2$ (L = pyrrolidine and R = butyl group) in nitrobenzene has been investigated. The rate constants for substitution of pyrrolidine by chloride ion, originating from different nucleophilic reagents such as C_6H_5COCl, $SOCl_2$ and CH_3COCl have also been calculated. A possible mechanism has been suggested.

Millimolar solution of the complex was prepared in nitrobenzene and variation in conductance was measured as a function of time. The plot of molar conductance, Λ_M versus time was a curve and from the slope of the linear portion of this curve specific rate constant for solvation, k_s was calculated to be $1.2 \times 10^{-6} s^{-1}$.

The nucleophile and the complex in nitrobenzene were mixed separately in three different molar ratios. The conductance of each solution was measured immediately and after regular 5 min interval for a period of 1 hr. The limiting conductance Λ_∞ was measured after 24 hr. The increase in conductance was faster in the presence of a nucleophile than in its absence. The molar conductance (Λ_M) versus time curve for substitution was similar to that obtained for solvation (Fig. 1).

On plotting $\log [\Lambda_\infty/(\Lambda_\infty - \Lambda_M)]$ against time a linear plot was obtained for different molar ratios of the reactants indicating that the reactions in the presence and absence of nucleophiles followed first order kinetics. In the substitution reaction by chloride ion two mutually intersecting linear plots were obtained (Fig. 2). The specific rate constants, k_1 and k_2 for stepwise replacement of pyrrolidine were calculated from the slope of the first and second linear portions of the plots respectively using the method of two mutually intersecting lines; the values of k_1 and k_2 are presented in Table 1. The integrated equation for calculation of first order rate constant is given by Eq. (1).

$$k = -\frac{2.303}{t} \log(\Lambda_\infty/\Lambda_\infty - \Lambda_M) \qquad \ldots (1)$$

In the absence of the nucleophile the magnitude of increase in molar conductance in the initial stage is low as compared to that in the presence of nucleophile. This may be due to the solvation of the complex (Eq. 2) followed by substitution of pyrrolidine by Cl^- (Eq. 4).

$$R_2SnCl_2L_2 + S \rightleftharpoons [R_2SnSClL_2]^+ + Cl^- \qquad \ldots (2)$$

$$R_2SnCl_2L_2 + S \rightleftharpoons R_2SnSCl_2L + L \qquad \ldots (3)$$

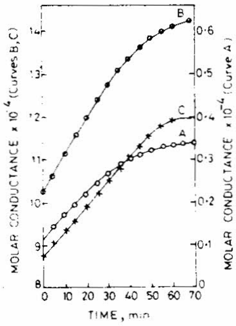

Fig. 1—Molar conductance versus time curves [(A) for solvation of $L_2R_2SnCl_2$ in nitrobenzene; (B) for substitution of $L_2R_2SnCl_2$ using CH_3COCl; and (C) for substitution of $L_2R_2SnCl_2$ using $SOCl_2$.

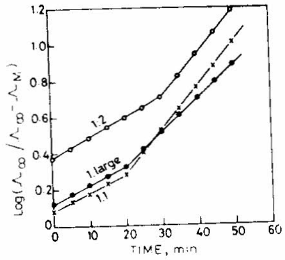

Fig 2—First order plots for substitution of $L_2R_2SnCl_2$ by C_6H_5COCl in different molar ratios.

Table 1—Rate Constant for Substitution of Pyrrolidine by Chloride Ion in the Complex $[R_2SnCl_2L_2]$

Nucleophilic reagent	Ratio	$k_1 \times 10^{-2}$ s^{-1}	$k_2 \times 10^{-2}$ s^{-1}
$SOCl_2$	1:1	2.8	7.2
	1:2	2.7	7.2
	1:large	2.8	7.1
C_6H_5COCl	1:1	2.3	5
	1:2	2.3	4.9
	1:large	2.5	5
CH_3COCl	1:1	1.4	3.9
	1:2	1.3	3.8
	1:large	1.4	3.9

$$R_2SnCl_2L_2 + Cl^- \rightleftharpoons [R_2SnCl_3L]^- + L \qquad \ldots (4)$$

The replacement of the stronger nucleophiles, i.e. the chloride ion and pyrrolidine by the solvent, nitrobenzene is due to the mass effect. The generation of pyrrolidine in step (3) suppresses the consumption of chloride ion in step (4), as a result of which the equilibrium is shifted in backward direction in reaction (2). Consequently, less ionic species are produced which decrease the rate of solvation. Since reactions (2) and (4) are fast reaction (3) becomes rate-determining.

It is clear from the rate of increase in conductance during substitution that the chloride ion is a strong nucleophile than pyrrolidine and nitrobenzene[5]. The mechanism in Scheme 1 is proposed for the substitution reaction.

$$R_2SnCl_2L_2 \rightleftharpoons [R_2SnCl_2L] + L \overset{Cl^-}{\rightleftharpoons} [R_2SnCl_3L]^-$$

$$R_2SnCl_3L^- \rightleftharpoons [R_2SnCl_3]^- + L \overset{Cl^-}{\rightleftharpoons} [R_2SnCl_4]^{2-}$$

Scheme 1

We believe that the stepwise replacement of the base molecule (L) by the chloride ion results in the formation of the species $[L-R_2SnCl_3]^-$ and $[R_2SnCl_4]^{2-}$ as final products. As a result the molar conductance of the solution increases with time and attains a limiting value after 24 hr. The dissociation of $[L-R_2SnCl_3]^-$, seems to be faster than that of $[L-R_2SnCl_2]$, because of the negative charge on the former. However, an equilibrium is attained after 24 hr.

It is concluded that the rate of substitution is faster than the rate of solvation. The substitution follows an S_N1 pathway. The nucleophilic reagents may be arranged in the decreasing order of the rate constants (k_1 and k_2) of nucleophilic substitution as follows: $SOCl_2 > C_6H_5COCl > CH_3COCl$.

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