

Kinetics and mechanism of nucleophilic substitution of acridine by chloride ion in octahedral tin(IV) complexes

K S Siddiqi*, Fathi M A M Aqra, S A Shah & S A A Zaidi

Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India

Received 3 June 1992; revised 15 September 1992; accepted 27 January 1993

The nucleophilic substitution of acridine by chloride ion in SnCl_4L_2 and $\text{R}_2\text{SnCl}_2\text{L}_2$ (where $\text{R} = \text{Me, Bu, Ph}$, and $\text{L} = \text{acridine}$) carried out in acetonitrile at ambient temperature follows first order kinetics. A millimolar solution of the complexes in acetonitrile shows increase in conductance with time indicating solvation which is enhanced in the presence of SOCl_2 , $\text{C}_6\text{H}_5\text{COCl}$ and CH_3COCl suggesting the replacement of acridine by chloride ion. The rate constants k_1 , k_2 and the thermodynamic parameters (activation energy, entropy, and enthalpy) have been calculated. The nucleophilicity of these reagents has been found to be in the order: $\text{SOCl}_2 > \text{C}_6\text{H}_5\text{COCl} > \text{CH}_3\text{COCl}$.

While the spectrophotometric method may be available for the study of the substitution reaction of some group (IV) metal complexes¹ the kinetics of substitution of compounds yielding colourless solution may be conveniently followed by conductometric method.

In the present paper, we have selected SnCl_4L_2 and $\text{R}_2\text{SnCl}_2\text{L}_2$ (where $\text{R} = \text{Bu, Me, Ph}$ and $\text{L} = \text{acridine}$) in order to examine the influence of the alkyl groups on the rate of substitution. In these complexes, the ligand is replaced by chloride ion liberated from different nucleophiles such as SOCl_2 , $\text{C}_6\text{H}_5\text{COCl}$ and CH_3COCl . The conductometric measurements were carried out on the solutions of the complexes in acetonitrile. Since increase in temperature makes negligible change in conductance, the experiments were done only at ambient temperature. The rate constants k_1 and k_2 for the successive replacement of acridine by Cl^- and the thermodynamic parameters (ΔG , ΔH and ΔS) have been calculated.

Materials and Methods

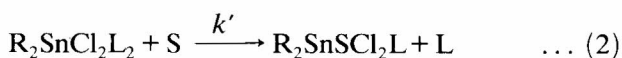
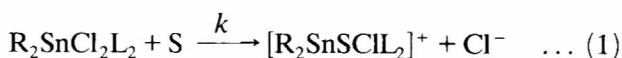
Millimolar solutions of the complexes were prepared in acetonitrile and their conductances were measured as a function of time. From the slope of the linear portion of a plot of molar conductance versus time, the rate constant (k) for solvation was found to be $7.6 \times 10^{-4} \text{ s}^{-1}$.

The solutions of the nucleophiles and the complexes were mixed separately in three different ratios. The conductance was measured immediately and after regular intervals over a period of one

hr. The limiting conductance (Λ_a), was measured after 24 hr.

Results and Discussion

The molar conductance (Λ_m) versus time curve for substitution was similar to that obtained for solvation (Fig. 1). However, the change in molar conductance in the former case was greater than in the latter. The probable mechanism for the solvation is outlined below:



where $\text{R} = \text{Me, Bu, Ph}$; $\text{L} = \text{acridine}$; $\text{S} = \text{solvent (acetonitrile)}$

During solvation, either the chloride ion or the ligand may be replaced by the solvent^{3,4} (Eqs 1 and 2). The smaller increase in molar conductance in the absence of the nucleophile may be ascribed only to the solvation of the complexes. The mechanism of solvation involving release of chloride ion and generating $[\text{R}_2\text{SnSClL}_2]^+$ species would have caused substantial increase in the conductance and therefore, ruled out. Hence, it is suggested that solvation is accompanied by the release of the ligand as shown by Eq. 2. However, when the nucleophile is added the conductance increases due to the substitution of acridine by chloride ion, liberated from the nucleophile.

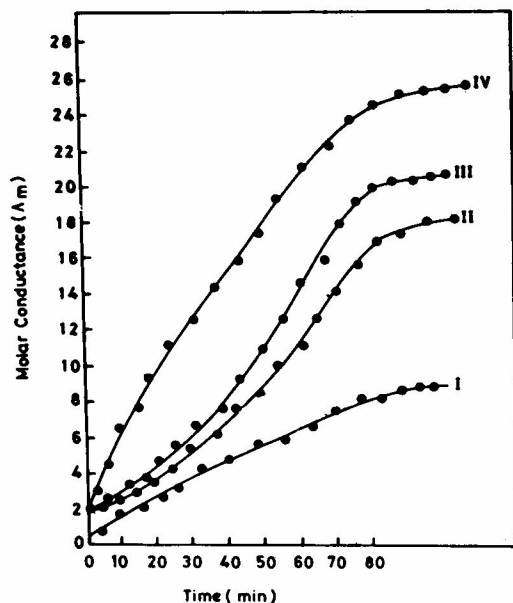


Fig. 1—Molar conductance-time curve for (R = Me, Bu, Ph) (I) in acetonitrile, (II) with CH_3COCl in acetonitrile, (III) with $\text{C}_6\text{H}_5\text{COCl}$ in acetonitrile, (IV) with SOCl_2 in acetonitrile.

Table 1—Rate constant for substitution of acridine by chloride ion in the complex $\text{L}_2\text{SnCl}_2\text{R}_2$ (R = Me, Bu, Ph)

Nucleophilic reagent	Ratio	$k_1 \times 10^2$ (s^{-1})	$k_2 \times 10^2$ (s^{-1})
SOCl_2	1 : 1	3.10	7.4
	1 : 2	3.10	7.4
	1 : large	3.10	7.4
$\text{C}_6\text{H}_5\text{COCl}$	1 : 1	2.6	7.2
	1 : 2	2.6	7.2
	1 : large	2.6	7.2
CH_3COCl	1 : 1	1.8	5.9
	1 : 2	1.8	5.9
	1 : large	1.8	5.9

Plot of $\log [\Lambda_a / \Lambda_a - \Lambda_m]$ against time (Fig. 2) was linear suggesting first order kinetics in the presence of nucleophiles. The values k_1 and k_2 for stepwise replacement of acridine by chloride ion were calculated from the slope of the first and second linear portions of the plots respectively, using the method of two mutually intersecting lines². Their values are listed in Table 1. The rate constants were calculated by the equation:

$$k = \frac{2.303}{t} \log (\Lambda_a / \Lambda_a - \Lambda_m)$$

The substitution may follow either SN_1 or SN_2 mechanism⁵. In the present case, it has been

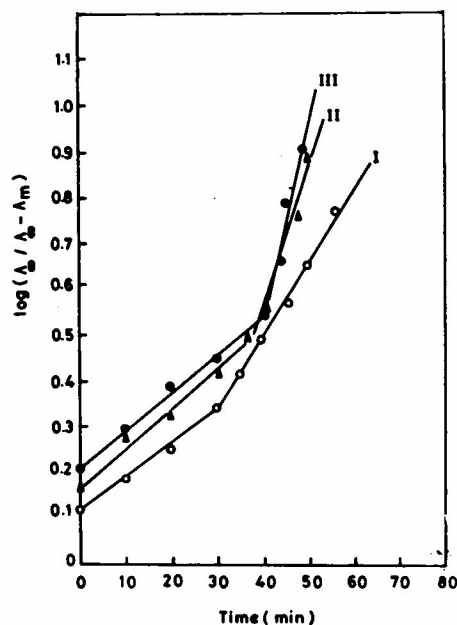
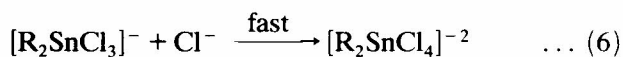
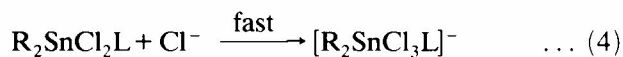


Fig. 2—First order plot for various nucleophilic reagents. I. CH_3COCl , II. $\text{C}_6\text{H}_5\text{COCl}$, III. SOCl_2 , for 1 : 2 complex.

Table 2—Thermodynamic parameters for first and second substitutions

Nucleophilic reagent	For first substitution		For second substitution	
	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (JK^{-1} mol^{-1})
SOCl_2	176.56	0.77	125.93	0.59
$\text{C}_6\text{H}_5\text{COCl}$	160.24	0.65	117.98	0.54
CH_3COCl	148.11	0.47	113.80	0.36

shown to follow SN_1 reaction for which the following mechanism in Scheme 1 has been proposed^{3,4,6}:



where R = Me, Bu, Ph

Scheme 1

The rate of increase in molar conductance during nucleophilic substitution is as expected since the chloride ion is obviously a stronger nucleophile than either acridine or the solvent⁷. The high nucleophilicity of the chloride ion is able to compete with the greater concentration of the solvent in the substitution reaction. There is bond breaking leading to the formation of five coordinate intermediate species⁸ (steps 3 and 5) followed by bond formation (steps 4 and 6). There are several such stable five coordinate compounds of R_3SnCl , $R_2Sn(AC)_2$ known with quinoline derivatives⁹. The mechanism proposed is also clear from Fig. 2 which consists of two intersecting lines indicating two different rate determining steps. Thus the dissociation of acridine by chloride ion in reactions (3) and (5) is a slow process and hence rate determining step. Breaking one of the two metal ligand bonds (3) followed by the attack of chloride ion results in the formation of $[R_2SnCl_3L]^-$. In the presence of high concentration of chloride ion (high concentration of nucleophile), the second M-L bond breaks (5) and M-Cl bond is formed yielding $[R_2SnCl_4]^{2-}$ as the final product (6). Consequently, the molar conductance as a function of time increases and attains the maximum value after 1 hr. The Λ_a was obtained after 24 hr. The reaction (4) is faster than reaction (6) due to the negative charge on the former. It is interesting to note that all the complexes show same results indicating no effect of steric hindrance of alkyl groups on the rate of substitution reaction.

By substituting the values of k_1 and k_2 in Arrhenius equation, the energy of activation, entropy and enthalpy has been calculated (Table 2). These support the SN1 mechanism and show that bond breaking is a slow, and hence, rate determining step.

From all these observations, we conclude that the rate of substitution is faster than the rate of solvation. In the absence of the nucleophile, the interaction with the solvent is greater. The substitution follows SN1 pathway. On the basis of the ΔS values the nucleophiles for substitution reaction may be arranged in the following descending order: $SOCl_2 > C_6H_5COCl > CH_3COCl$.

Acknowledgement

The authors are thankful to Rasheed Jamhour for his assistance in conductivity measurements.

References

- 1 Wang X, Liu X, Zhang Z & Liang S, *Hauxue Xuebao*, 45 (1987) 938.
- 2 Pearson R G, Meeker R E & Basolo F, *J Am chem Soc*, 78 (1956) 2673.
- 3 Sandhu S S & Bhatia J C, *J inorg nucl Chem*, 31 (1969) 2445.
- 4 Chettalini L, Chessa G, Michelon G, Pitteri B, Tobe M L & Zanardo A, *Inorg Chem*, 24 (1985) 3409.
- 5 Margeum D W & Margenthaler L F, *J Am chem Soc*, 84 (1962) 706.
- 6 Lynne Richards, *J chem Educ*, 65 (1988) 82.
- 7 Sandhu S S & Singh A, *J Indian chem Soc*, 42 (1965) 744.
- 8 Beattie I R & Gilson T, *J chem Soc*, (1961) 2585.
- 9 Siddiqi K S, Zaidi F R, Khan T A & Zaidi S A A, *Bull Soc Chem (France)*, I (1983) 140.