

The Effect of 'R' Group in *Bis* (N-R, Salim) Nickel (II) on the Dehalogenation of Chloroform

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The study of the effect of 'R' group on the dehalogenation of chloroform prompted by the ligand substitution reaction system, consisting of *bis* (N-R, salim) nickel (II) (with R=H, CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, s-C₄H₉, t-C₄H₉) and N,N,N',N'-tetramethylethylenediamine has been carried out. The kinetics study has been followed by the measurement of rate of chloride release at five different temperatures. It has been observed that both, the basicity and geometrical characteristics of the R group control the kinetics of dehalogenation. A relationship between Taft substituent parameter of the R group and energy of activation has been observed. The deviation observed from this relation (R=H) has been attributed to the geometrical factors. The nature of the proposed intermediate has been substantiated by showing a correlation between the energy of activation and the downfield chemical shift of the methine proton. The data of activation entropy and enthalpy changes follow the isokinetic relationship, indicating the importance of the structural factors of the Schiff base complexes in the dehalogenation reaction.

It has been reported¹ that the anine exchange reaction between *bis* (N-n-butyl, salim) nickel(II) and diamines in chloroform involves a dehalogenation reaction of chloroform. An activated complex containing nickel(II) with seven coordination number has been proposed. This work will have to be substantiated by determining the kinetics data using *bis* (N-R, salim) nickel (II) with R having different basicity and geometrical configuration. The present work reports such kinetics data using *bis* (N-R, salim) nickel (II) with R=H, CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, s-C₄H₉, t-C₄H₉.

Experimental

The conventional procedures² were used for synthesis of Schiff base complexes of nickel(II), *bis* (N-R, salim) nickel (II) (with R=H, CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, s-C₄H₉, t-C₄H₉). The complexes were tested for purity by determining i.r. spectra, elemental analysis and melting point^{3,4}. The i.r. spectra were determined using nujol and hexachlorobutadiene mulls on Beckman IR-4 spectrophotometer. The e.m.f. measurements were done on Radiometer PHM 4a pH meter.

For the kinetics measurements, a three-necked flask (300 ml) was equipped with a reflux condensor, glass electrode and silver-silver chloride electrode. The experimental solution (200 ml) was poured into this flask and maintained at a specific temperature ($\pm 0.1^\circ$) by using the oil thermostat. The experimental solution was prepared in a 250 ml volumetric flask by mixing 120 ml of chloroform solution of *bis* (N-R, salim) nickel (II) ($0.250 \times 10^{-3} M$) and 120 ml of N,N,N',N'-tetramethylethylenediamine ($8.58 \times 10^{-3} M$) in methanol, and adjusting the total volume to 250 ml using methanol-chloroform mixture (1:1 V/V).

The pseudo-first order rate constants, k , were calculated by using the equation, $k = 2.303 m$; here m is the slope of the linear plot of $-\log (V_\infty - V_t)$ vs time, t (in seconds); V_t and V_∞ are the potentials across the electrodes of the experimental solution at time t , and at the end of the reaction. The thermodynamic constants of the reaction—the energy of activation and the enthalpy and entropy of activation—were calculated by using the usual equations.

Results and Discussion

The results are summarized in Table I.

In the dehalogenation of chloroform by a Schiff base complex, *bis* (N-R, salim) nickel (II), the chelate exchange reaction is the rate determining step. (Eqn. 1). It is obvious that, the basicity of R group and the geometry of the original complex will affect the rate of reaction. In solution, the complexes, *bis* (N-R, salim) nickel (II) are square planar with R=H, and are compressed tetrahedral with R=n-C₃H₇, n-C₄H₉, s-C₄H₉ and t-C₄H₉⁵; with R=CH₃ and C₂H₅ there is an equilibrium between the square planar and tetrahedral configurations⁶. These changes in the geometry are related both to the size and the electronic effect of the R group.

The geometrical changes in the complex molecules, due to these factors will change the nature of hybrid atomic orbitals on oxygen, participating in metal-oxygen coordination⁷. It is therefore logical to expect a correlation between the activation energy of the dehalogenation reaction under consideration and the electronic properties of the substituent R, after giving due considerations to the geometrical factors of group R.

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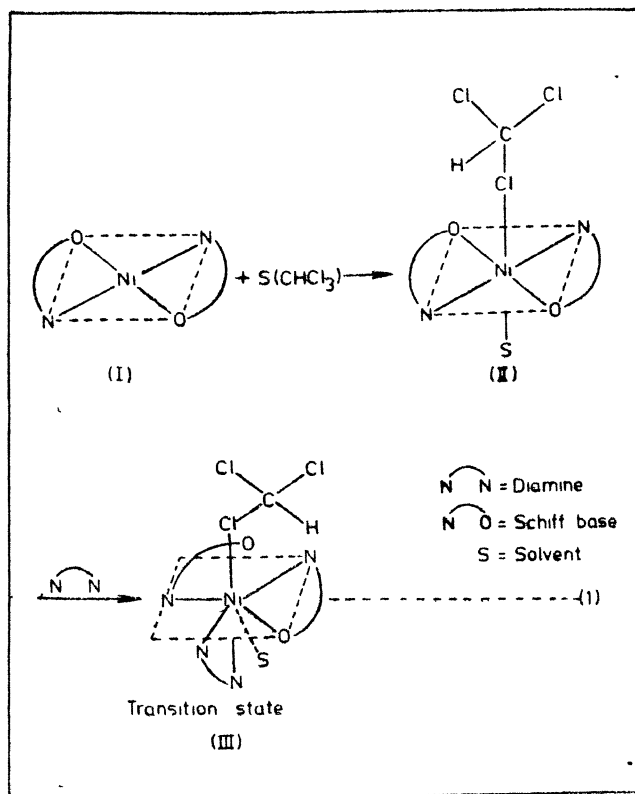
TABLE 1—KINETICS OF DEHALOGENATION OF CHLOROFORM

Complex*	Temp., °C	Pseudo- first order rate constant (sec ⁻¹) $k \times 10^4$	Energy of activation (kcal/mole)	Entropy of activation (e.u.)	Enthalpy of activation (kcal/mole)	Chemical shift δCH (ppm***)
1. <i>Bis</i> (N-ter- butyl, salim) nickel (II) (-0.30)	60	0.90	18.4 ± 0.1	-23.8	17.7 ± 0.1	8.21
	63	1.40				
	67	2.10				
	71	3.00				
	75	3.25				
2. <i>Bis</i> (N-Sec- butyl, salim) nickel (II) (-0.21)	60	1.05	17.5 ± 0.1	-26.7	16.8 ± 0.1	8.20
	63	1.60				
	67	2.25				
	71	3.20				
	75	3.40				
3. <i>Bis</i> (N-n-butyl, salim) nickel (II) (-0.13)	60	1.20	16.1 ± 0.1 $(17.2 \pm 0.6)**$	-31.0 $(-27)**$	15.4 ± 0.1 $(16.5 \pm 0.6)**$	8.15
	63	1.87				
	67	2.40				
	71	3.50				
	75	3.65				
4. <i>Bis</i> (N-n- propyl, salim) nickel (II) (-0.115)	60	1.80	13.8 ± 0.1	-37	13.1 ± 0.1	8.16
	63	2.10				
	67	2.70				
	71	3.60				
	75	4.10				
5. <i>Bis</i> (N-ethyl, salim) nickel (II) (-0.110)	60	2.10	10.0 ± 0.1	-47.9	9.3 ± 0.1	8.06
	63	2.60				
	67	3.00				
	71	3.70				
	75	4.20				
6. <i>Bis</i> (N-methyl, salim) nickel (II) (0.000)	60	2.60	6.9 ± 0.1	-56.9	6.2 ± 0.1	8.01
	63	2.80				
	67	3.40				
	71	3.84				
	75	4.45				
7. <i>Bis</i> (N-H, salim) nickel (II) (+0.490)	60	2.80	5.9 ± 0.1	-59.7	5.2 ± 0.1	
	63	3.30				
	67	3.60				
	71	4.00				
	75	4.50				

* The quantities given in brackets in the first column are the Taft substituent parameters of the R group.

** D. F. Martin, *J. Inorg. Nuclear Chem.*, 1975, 37, 1941.

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polarization effect of the substituent, indicates that the point corresponding to R=H has a large deviation from this representation. If the basicity of the R group was the only factor deciding the kinetic aspects of the dehalogenation reaction, a uniform correlation between Taft substituent parameter and energy of activation would have been obtained. The experimental observations indicate that the geometrical factors are of equal importance. It may be suggested here that Taft substituent parameters depend on geometry.

In tetrahedral geometry, the hybridization of the atomic orbitals on oxygen will be of sp^3 type which will have better overlap with the metal orbitals. The energy of activation for the dehalogenation reaction using tetrahedral complexes will therefore be higher than that using the square planar complexes.

The change in electron density on nitrogen and oxygen of a Schiff base due to the hyperconjugative effect of R group will be reflected on the downfield chemical shift of the methine proton⁹. As we have seen above, the electron density at oxygen and nitrogen controls also the activation energy of dehalogenation reaction. The favourable hyperconjugative effect of the R group will increase the electron density on coordinating nitrogen and oxygen, and will deshield the methine proton. A higher energy of activation is, therefore, expected for a compound having a higher value of the methine proton chemical shift. The experimental observations are according to this prediction (Fig 2).

A graphical representation between the energy of activation of dehalogenation reaction and Taft substituent parameter⁸ which is the measure of the electronic

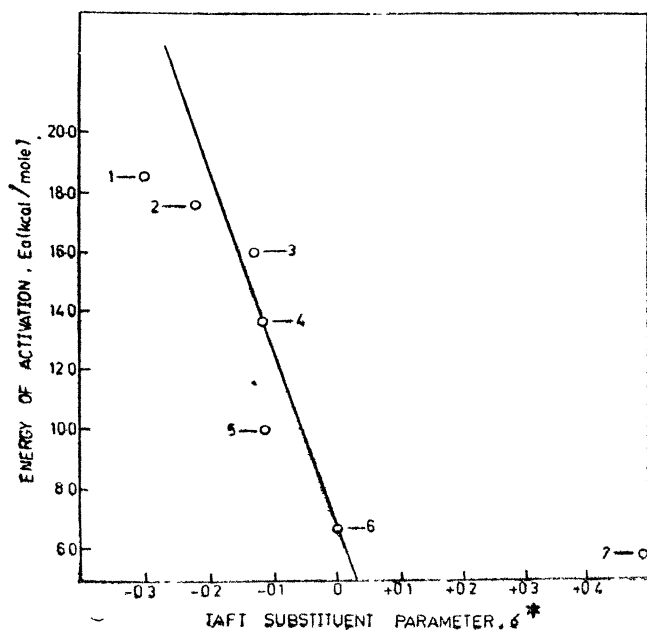


Fig. 1. Relationship between energy of activation and Taft substituent parameter for the ligand substitution reaction of *bis* (N-R, Salim) nickel (II).

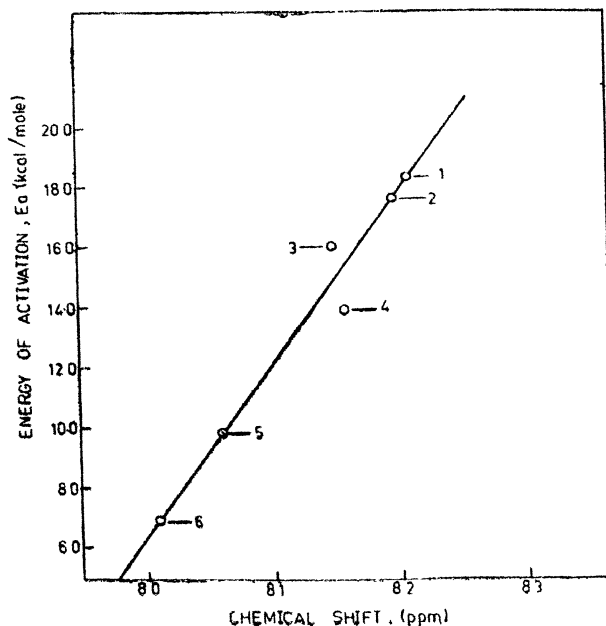


Fig. 2. Relationship between downfield chemical shift of the methine proton (in $CDCl_3$ relative to TMS) and energy of activation for the ligand substitution reaction of *bis* (N-R, salim) nickel (II).

It is interesting that an excellent isokinetic relationship^{10,11} has been observed between the activation

entropy change (ΔS^\ddagger) and activation enthalpy change (ΔH^\ddagger) of the dehalogenation reaction (Fig. 3). This observation suggests that both ΔH^\ddagger and ΔS^\ddagger are decidedly dependent on the structure of the reaction intermediate^{1,2}. The effect of changing R on ΔH^\ddagger is proportional to the effect on ΔS^\ddagger .

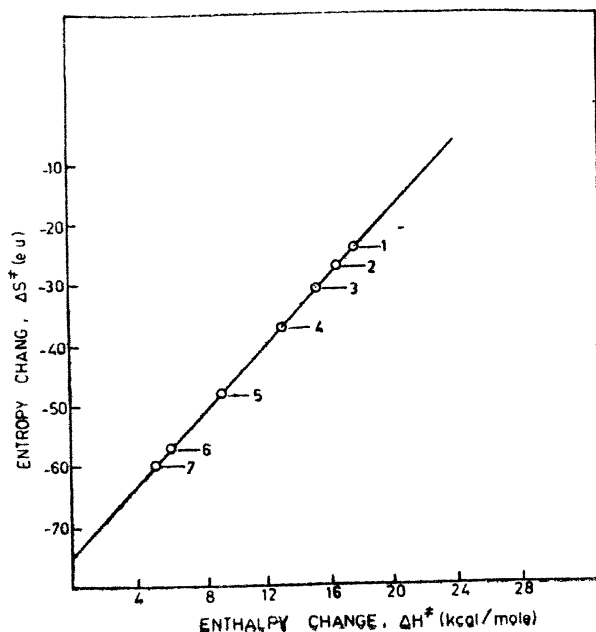


Fig. 3. Isokinetic relationship for the ligand substitution reaction of *bis* (N-R, salim) nickel (II).

For all the systems studied in the present work ΔS^\ddagger is negative. This supports the proposed activated complex which takes up one more ligand from the medium. The solvation also contributes to the negative change in entropy. It seems that the entropy change depends on the R group; lower the value of Taft substituent parameter lower is the value of entropy change. It has been also observed that a reaction having higher activation energy has less negative entropy change.

To summarise, the present kinetics study substantiates the mechanism for the dehalogenation reaction of chloroform involving the addition intermediate. The magnitude of the energy of activation depends on the contribution of the R group to the hyperconjugative effect and the geometry of the ground state of metal complexes in solution.

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