

TRANSFORMATION OF Ni[HSAL-N-ALKYL]₂* COMPLEXES IN THE PRESENCE OF AMMONIUM SALTS (Short Communication)

By

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The kinetics of the transformation Ni[HSAL-N-alkyl]₂ → Ni[HSAL-NH]₂ in the presence of an ammonium salt was studied, and the factors influencing the reaction rate were investigated in detail.

The kinetics of formation of Schiff base chelates from Ni[HSAL]₂ and primary amines [1] and the kinetics of the amine-exchange reactions of metal chelates [2–4] have been reported in numerous papers. We earlier [5] demonstrated that the Ni[HSAL-N-alkyl]₂ complexes (alkyl = n-butyl, hexyl, dodecyl) undergo transformation in alcoholic or acetonic solution in the presence of water and ammonium salts (NH₄X, X = Cl⁻, Br⁻, I⁻, NO₃⁻, SCN⁻, SO₄²⁻). As the end-product of the reaction, Ni[HSAL-NH]₂ may be isolated as well-defined crystals; these results were supported by spectrophotometric and polarographic measurements. It was found that the reaction takes place between the N-alkyl derivatives and NH₄-salts, but no change could be observed for the N-phenyl derivatives or with other salts (e.g. KCl, NaCl, LiI, tetraalkyl-ammonium halides). The transformation can readily be followed spectrophotometrically, for the colour of the solution changes during the processes from deep-green to red-brown; the intensity of the band of the N-alkyl derivative decreases and simultaneously the characteristic band of the imine chelate (see e.g. Fig. 1) gradually develops.

This paper reports new results on the reaction of Ni[HSAL-N-alkyl]₂ complexes (alkyl = C₂–C₇) in NH₄NO₃/acetone/water systems. The complexes

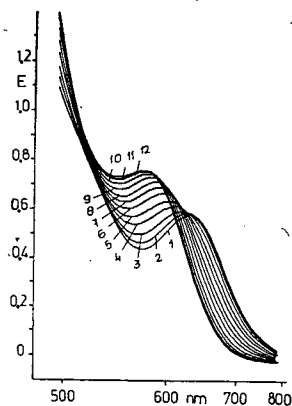


Fig. 1. Change of spectrum of the Ni[HSAL-N-*n*-C₄H₉]₂ + NH₄NO₃ system with time in acetone at 298 K. [chelate] = 0.01, [salt] = 0.06 mol/dm³; d = 0.1 cm. t = 1: 0; 2: 4; 3: 10; 4: 20; 5: 30; 6: 4; 5; 7: 60; 8: 80; 9: 110; 10: 150; 11: 200; 12: 260 min.

* HSAL = salicylaldehyde anion.

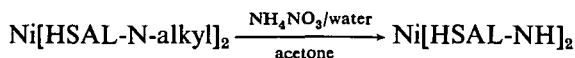
Table I

Values of first-order rate constants for reactions of Ni[HSAL-N-alkyl]₂ complexes with NH₄NO₃ in acetone at 298 K

Alkyl=	[Chelate]. 10 ⁻²	[Salt]. 10 ⁻²	[Water]. 10 ⁻²	k · 10 ⁻² (min ⁻¹)
ethyl	1	6	1	7.67
<i>n</i> -propyl	1	6	1	4.73
<i>i</i> -propyl	1	6	1	3.43
<i>n</i> -butyl	1	4	1	2.69
	1	6	1	4.30
	1	6	2.7	4.40
	1	6	3.3	4.66
	1	6	4.0	4.84
	1	6	5.3	5.75
	1	6	6.7	6.37
	1	8.4	1	6.48
	1.5	4	1	2.38
	1.5	6	1	4.08
	1.5	8.4	1	6.10
	2	4	1	2.02
	2	6	1	3.74
	2	8.4	1	5.66
	2.5	4	1	1.56
	2.5	6	1	3.48
	2.5	8.4	1	5.22
<i>i</i> -butyl	1	6	1	4.55
<i>n</i> -amyl	1.5	4	1	3.35
<i>i</i> -amyl	1	6	1	5.63
<i>n</i> -hexyl	1	6	1	4.26
<i>n</i> -heptyl	1	6	1	3.69

studied were prepared as reported in the literature [e.g. 6]. The NH₄NO₃ was Merck p.a., while the solvents were of the spectroscopic grade of purity. Separate solutions of the complexes and the salt were prepared in acetone**. After mixing of appropriate amounts of the solutions, the kinetics was followed *via* the absorption changes in the visible, between 340 and 700 nm. Kinetic calculations were performed at the wavelength showing the largest absorption variation between the starting and the final spectra. The final spectrum was always identical with that of Ni[HSAL-NH]₂. The first-order rate constants *k* (min⁻¹) determined under various conditions are reported in Table I.

It is well known that the solutions of these alkyl derivatives show no change on standing or in the presence of water or different salts. However, ammonium salts have a considerable effect on the parent N-alkyl compounds; the following reaction takes place:



From a study of the rate constants in Table I the following conclusions may be drawn.

** The acetic solution of NH₄NO₃ contains a known amount of water.

1. The rate constant varies with the length of the N-*n*-alkyl chain. This change is similar to that observed between the equilibrium constant of the dia/para equilibrium in the CHCl₃/pyridine system and the number of carbon atoms in the *n*-alkyl chain [7].

2. If [chelate]=[salt], the reactions are very slow. If [chelate]=const. or [salt]=const., the rate constant increases ($\tan \alpha \approx 0.9$) or decreases ($\tan \alpha \approx -0.6$) linearly, respectively, with the increase in concentration of the reaction partner.

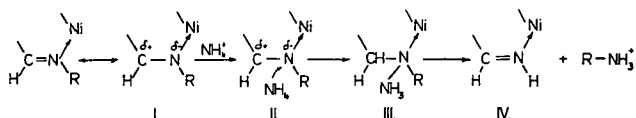
3. The rate of the reaction depends strongly on the water concentration; the plot of *k* against the water concentration is linear ($\tan \alpha \approx 0.5$). In the absence of water, essentially no change can be observed during several days.

4. Ni[HSAL-NH]₂ and the corresponding alkylammonium hydrochloride can be isolated from the solution in every case.

5. The rate constants for the branched alkyl derivatives increase in the sequence $i-C_3H_7 < i-C_4H_9 < i-C_5H_{11}$.

6. No isosbestic point was observed in the region studied, which proves the accumulation of the intermediate III.

We assume that in transformation in question the NH₄⁺ ions play an important role, and we propose the following reaction scheme.



This mechanism involves reactions beginning with electrophilic attack by NH₄⁺ on the azomethine nitrogen (II), leading to the intermediate III. The azomethine linkage is polarized as a result of coordination, and thus the electron-rich nitrogen would be susceptible to attack. It seems that the strength of the Ni—N bond is an important factor. If this bond is particularly strong, the transformation is less likely, and *vice versa*. A proton transfer to the azomethine carbon and subsequent cleavage of R—NH₃⁺ leads to the formation of the imine complex IV.

A detailed discussion of this mechanism will be published in a forthcoming paper.

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ПРЕВРАЩЕНИЯ КОМПЛЕКСОВ ТИПА Ni[HSal-N-alkyl]₂ В ПРИСУТСТВИИ СОЛЕЙ АММОНИЯ (Краткое сообщение)

Й. Часар

На основании изучения превращений комплексов типа Ni[HSal-N-alkyl]₂ в присутствии солей аммония предложена простая схема механизма происходящих явлений.

