

Isotopic exchange study of nickel xanthate in the presence of toluidines

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MS received 30 December 1977; in final form 5 July 1978

Abstract. Isotopic exchange behaviour of nickel xanthate is studied in presence of three isomeric toluidines at 25° C. The results show that the complex becomes labile in the kinetic sense in presence of *m*- and *p*-toluidines. The complex displays inert behaviour in the presence of *o*-toluidine and it is ascribed to dominant steric effect.

Keywords. Nickel xanthate; toluidines; isotopic exchange.

1. Introduction

Isotopic exchange study of nickel xanthate has shown that the complex is non-labile in the kinetic sense. Exchange study repeated in the presence of aniline has revealed that the complex is labile in character (Rangamannar 1977). The lability of the complex has been ascribed to the formation of an adduct with aniline. Further, the adduct formation leads to the transition from the diamagnetic, square planar, four coordinate nickel complex to paramagnetic bis adduct as reported by Lim Yau Yan (1974). This leads support to the lability observed in the presence of aniline. However, no effort has been made so far to study the behaviour of nickel xanthate in presence of substituted anilines. Hence isotopic exchange results relating to the behaviour of nickel xanthate in presence of the three isomeric toluidines are presented here. The results have been interpreted in terms of the differences in basicities and geometrical factors of the three toluidines.

2. Experimental

2.1.

Potassium ethyl xanthate was prepared by the method described by Vogel (1951).

2.2. Preparation of the complex

The complex was prepared by the method reported by Dakterneiks and Graddon (1971) with a slight modification. In the present work the complex was prepared in aqueous medium. The pH of nickel solution (1 mM) was adjusted to 8.0-8.5. A

1% solution of potassium ethyl xanthate was added with constant stirring until the precipitation was complete. The resulting precipitate was filtered, washed with hot water and dried in vacuo. Estimation of nickel by a conventional method showed that the complex had metal to ligand ratio of 1 : 2 as observed by Dakterneiks and Graddon (1971).

2.3. Chemicals

Acetone (BDH) AnalaR sample was used without further purification. Nickel perchlorate (AnalaR) was used.

Ortho, meta and para toluidines (BDH) were purified by the method described by Naidu (1963). The purity of the compounds was ascertained by comparing the measured densities with those reported in the literature.

2.4. Exchange procedure

Solutions of nickel perchlorate (0.8752×10^{-2} M), nickel xanthate (0.8252×10^{-2} M) and toluidine (2×10^{-1} M) were prepared in acetone. Each reaction mixture consisted of 10 ml of the nickel perchlorate, 10 ml of the complex and 5 ml of base. The mixture was maintained at $25.0^\circ \text{C} \pm 1^\circ \text{C}$ and sufficient amount of ^{63}Ni tracer (200 λ) was added. The separation of the complex from free nickel was effected precipitating the former by the addition of 3 ml of water to a 2 ml aliquot of the reaction mixture at different time intervals. The radioactivity of the separated free nickel solution was measured with a liquid scintillation counter type: LSS 20 supplied by ECIL, Hyderabad. The course of the exchange was followed by measuring the activity as a function of time. The half time and the rate of exchange were calculated with the aid of McKay's relation (Wahl and Bonner 1951).

3. Results

Smooth exchange was observed in presence of meta and para toluidines and no exchange was observed in presence of *o*-toluidine. The relation

$$F = \frac{S_{At} - S_{Ao}}{S_{A\infty} - S_{Ao}}$$

was employed to compute fraction exchanged. In the relation S_{Ao} , S_{At} and $S_{A\infty}$ denote the specific activity of A, nickel perchlorate, separated at time 0, t and ∞ minutes respectively. F denotes fraction exchanged. Experimental data are given in table 1.

The accuracy of F depends upon uncertainty in the count rate. Count rate includes 1% error. This error introduces an uncertainty in the second decimal place of F value. Hence the value of F is presented to second decimal place.

The $t_{1/2}$, time necessary for the fraction of the exchange to reach a value of one

Table 1. Isotopic exchange data in presence of *o*-, *m*- and *p*-toluidines.

Time mts.	Counts/ mts.	<i>F</i>	1- <i>F</i>
<i>ortho toluidine</i>			
0	26674	—	—
15	26662	—	—
40	26432	—	—
85	26719	—	—
130	26002	—	—
175	26443	—	—
250	26482	—	—
325	26212	—	—
485	26386	—	—
∞	26502	—	—
<i>meta toluidine</i>			
0	24829	—	—
20	21129	0.48	0.52
35	18317	0.85	0.15
50	17520	0.95	0.05
60	17490	0.96	0.04
70	17352	0.98	0.02
80	17245	0.99	0.01
∞	17168	—	—
<i>para toluidine</i>			
0	22600	—	—
15	22033	0.08	0.92
45	20898	0.24	0.76
90	19941	0.38	0.62
170	19069	0.50	0.50
230	18856	0.53	0.47
280	18523	0.58	0.42
∞	15510	—	—

Table 2. Half times of exchange and exchange rates

Complex: 3.5×10^{-3} M Ni (II) : 3.3×10^{-3} M Base : 4×10^{-2} M.

	$t_{1/2}$ (min)	$R \times 10^5$ moles/litre/min
<i>m</i> -toluidine	11	10.7
<i>p</i> -toluidine	249	0.5

half was calculated from the values of $1-F$ and t by least squares method. Finally the rate R , was computed by the relation

$$R = \frac{\ln 2}{t_{1/2}} \cdot \frac{(A)(B)}{(A)+(B)}$$

where (*A*) and (*B*) are the concentrations of the complex and free nickel. Half times of exchange and the rate are given in table 2.

4. Discussion

The data included in table 2 shows that of the three isomeric toluidines, meta and para toluidines render nickel xanthate labile in the kinetic sense while ortho isomer fails to do so. The lability of the complex in presence of meta and para toluidines suggests that the complex forms adducts with the two bases as has been reported for other bases by Lim Yau Yan (1974) and Dakterneiks and Graddon (1971). The inert behaviour of the complex in presence of *o*-toluidine may be attributed to the steric effect of the methyl group. Methyl group in *o*-toluidine is capable of releasing electrons inductively and also it tends to form an intra-molecular hydrogen bond. While the former effect of methyl group leads to an increase in electron density of nitrogen, the latter effect reduces electron density. The observed exchange behaviour of nickel xanthate shows that the latter effect dominates and consequently *o*-toluidine may not be able to form an adduct with the complex.

Finally, the rates of exchange observed in the presence of meta and para toluidine fall in the order para < meta. This shows that the latter forms a stronger adduct than the former.

Acknowledgements

The authors gratefully acknowledge the facilities offered by Prof. M V Ramanaiyah, Head, Radio Chemistry Division, BARC, Bombay. The valuable suggestions given by Dr S K Patil, Radio Chemistry Division of BARC, Bombay are also gratefully acknowledged.

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