Preliminary communication

The isomerization of (benzyl thiocyanate)chromium tricarbonyl to isothiocyanate

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The most common mechanism for isomerization of organic thiocyanates to isothiocyanates, R—SCN → R—NCS, involves ionization[*] and the close parallelism between the capacity of organic moiety to support a positive charge and the ease of isomerization is clearly indicated by the behaviour of arylmethyl derivatives. Thus, while the isomerization of trityl thiocyanate is so fast even in solvents of low polarity that only the isothiocyanate can be isolated[2], benzhydryl thiocyanate isomerizes cleanly and easily in dipolar aprotic solvents at accessible temperatures (0—100°)[3], and benzyl thiocyanate isomerizes only in the presence of catalysts[4] or thiocyanate ion[5].

One of the most effective groups for stabilizing a benzyl cation is π-complexed tricarbonylchromium. Thus, the rate of solvolysis of (benzyl chloride)chromium tricarbonyl is increased by a factor of 10^5 compared to the uncomplexed benzyl chloride[6] and pK_{R+} values indicate that the benzyl cation complexed with $Cr(CO)_3$ is as stable as the benzhydryl cation[7]. The unusual capacity of the π-chromium tricarbonyl group to stabilize a positively charged α-carbon atom has now been tested applied to the isomerization of complexed benzyl thiocyanate.

(Benzyl thiocyanate)chromium tricarbonyl was prepared from (benzyl chloride)-chromium tricarbonyl and ammonium thiocyanate in anhydrous acetone. It is a yellow, air stable solid (m.p. 90—90.5°) readily soluble in both polar and non polar organic solvents. (Found: C, 46.02; H, 2.55; N, 4.94; S, 10.98; $C_{11}H_7CrNO_3S$ calcd.: C, 46.35; H, 2.45; N, 4.91; S, 11.22%) The infrared spectrum confirmed the presence of the thiocyanate group (2140 cm^{-1}) and the absence of the band characteristic of the isothiocyanate (2075 cm^{-1}).

The isomerization of (benzyl thiocyanate)chromium tricarbonyl was carried out in acetone at 65—85° under nitrogen. First-order rate constants, k_{is}, obtained by analyzing the samples for isothiocyanate by infrared spectroscopy are presented in Table 1.

(Benzyl thiocyanate)chromium tricarbonyl isomerizes in acetone at a rate, comparable with that for benzhydryl thiocyanates[3]. The rate is sensitive to the

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[*]For a review on the isomerization of organic thiocyanate, see ref. 1.

TABLE 1

FIRST-ORDER RATE CONSTANTS FOR THE ISOMERIZATION OF (BENZYL THIOCYANATE)-CHROMIUM TRICARBONYL IN ACETONE [a]

Temp. (°C)	Salt	[Salt]	$10^5\ k_{is}$ (sec^{-1}) [b]
85			4.7
85	NaClO$_4$	0.05	8.4
85	NaClO$_4$	0.10	12.9
75	NaClO$_4$	0.10	4.0
65	NaClO$_4$	0.10	0.9 [c]
85	NaSCN	0.10	10.8
85	LiClO$_4$	0.10	9.2

[a] Initial concentration 0.03 M. [b] Average of two or three different runs. [c] Arrhenius parameters in acetone/NaClO$_4$ 0.1 M: E_a = 32.2 kcal/mole; log A = 16.2.

addition of salts: the b value of Winstein's equation for normal salt effect is 17 for NaClO$_4$, a value fairly similar to that found for the same salt *viz.* 11.7, in isomerization of benzhydryl substrates. Sodium thiocyanate and lithium perchlorate appear to be only slightly less efficient in promoting the reaction and the differences lie within the limits of the specificity of different salts.

It is likely that π-complexed benzylthiocyanate isomerizes by way of a rate-determining ionization. Comparison of the rates of isomerization of (benzyl thiocyanate)chromium tricarbonyl and benzhydryl thiocyanate (k_{is} = 1.4 x 10^{-5} sec^{-1}) in acetone shows that the ratio k(complexed benzyl)/k(benzhydryl) is ca. 3.4 which is close to the value of 3.1 obtained for the solvolysis of the corresponding chlorides[6]. It is also in accord with the correlation between the thermodynamic stabilities of the carbonium ions and the rates of solvolysis[7].

A direct comparison with the uncomplexed thiocyanate is not feasible. The isomerization rate for this substrate is unmeasurably slow and only an upper limit of k_{is} was reported by Fava[5]. In methyl ethyl ketone with 0.1 M NaClO$_4$ at 110°, k_{is} is < 0.2 x 10^{-6} sec^{-1}. By using the value of the activation energy reported in Table 1, the first-order rate for the π-complexed benzyl thiocyanate in acetone/NaClO$_4$ 0.1 M at 110° can be calculated to be 5 x 10^{-3} sec^{-1}. Thus neglecting the difference in solvent (methyl ethyl ketone and acetone), the lower limit to the value of the ratio k_{is}(complexed)/k_{is}(uncomplexed) *i.e.* 2.5 x 10^4, represents a lower limit to the capacity of the π-Cr(CO)$_3$ group to stabilize the transition state of the isomerization.

Detailed studies on the mechanism of isomerization of π-Cr(CO)$_3$ complexed thiocyanates are in progress.

ACKNOWLEDGEMENT

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