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A Marvelous Catalysis of Tellurium in the Formation of Isothiocyanates from Isocyanides and Sulfur

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Abstract: Catalytic activity of tellurium in the formation of isothiocyanates from isocyanides and sulfur has been found to be extremely high and far superior to that of selenium.

Development of new synthetic reactions utilizing characteristics of tellurium has recently attracted much attention.[1] Reported herein is marvelous catalytic activity of elemental tellurium in the synthesis of isothiocyanates **1** from corresponding isocyanides and elemental sulfur (eq 1).

$$\mathrm{RNC} + \mathrm{S} \xrightarrow[\mathrm{THF,\ reflux}]{\mathrm{Te(cat.),\ Et_3N}} \underset{\mathbf{1}}{\mathrm{RNCS}} \qquad (1)$$

Although the simplest and the most straightforward access to isothiocyanates is the reaction of sulfur with isocyanides, several attempts for this purpose have never given satisfactory results.[2-5] Recently, we have reported that selenium possesses high catalytic activity in the formation of isothiocyanates from isocyanides and sulfur *via* Se-S exchange between sulfur and isoselenocyanates generated in situ as intermediates.[6] This successful result led us to examine catalytic activity of tellurium, another homologous element of sulfur.

To a mixture of elemental sulfur (3 mmol) and tellurium (0.125 mmol, 5 mol% to isocyanide) and triethylamine (6 mmol) in THF (5 mL) was added cyclohexyl isocyanide (2.5 mmol), and the mixture was refluxed for 1.5 h. Glc analysis of the resulting mixture showed that cyclohexyl isocyanide was completely consumed and cyclohexyl isothiocyanate **1a** was formed in 93 % yield (Table 1, run 1). In contrast to the case of selenium where **1a** was also obtained in high yield under similar conditions (run 2), it is particularly noticeable that the reaction mixture was heterogeneous throughout the reaction period, *i.e.*, most of tellurium

used remained unchanged suggesting that only a small portion of tellurium holds sufficient activity to convert the isocyanide. So the amount of tellurium catalyst was reduced step by step, and we have found that tellurium has marvelous catalytic activity. For example, even when 0.01 mol% of tellurium was used, **1a** was obtained quantitatively by prolonging the reaction period to 4 h (run 7). On the contrary, the reaction without tellurium catalyst hardly proceeded (run 3).

Table1. Tellurium Catalysis in the Formation of Cyclohexyl Isothiocyanate **1a**.[a)]

entry	Te, mol%	time, h	yield, %[b)]
1	5	1.5	93
2	5(Se)	2	95
3	—	1.5	2
4	0.5	1.5	97
5	0.05	1.5	99
6	0.02	2.5	99
7	0.01	4	99

a) Cyclohexyl isocyanide (2.5 mmol), S (3 mmol), Et_3N (6 mmol), THF (5 mL), reflux.
b) Glc yield.

The yields of **1a** versus reaction time at 50°C in the presence of 0.5 mol% of tellurium or selenium catalyst are given in Figure 1[7], which clearly shows the catalytic activity of tellurium to be far superior to that of selenium.

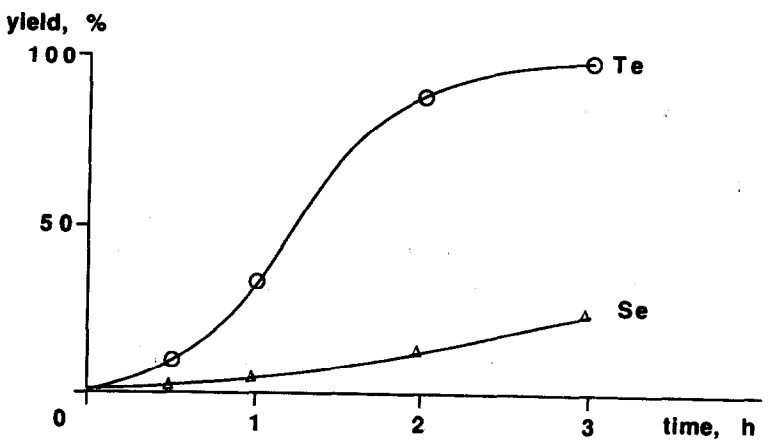


Figure 1. Time course of Te and Secatalyzed isothiocyanate formation.

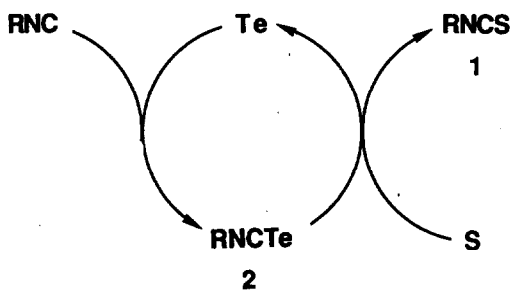
The results obtained with several isocyanides employed by using 0.02 mol% of tellurium catalyst are presented in Table 2. High to excellent yields were attained in any cases.

Table 2. Tellurium Catalyzed Formation of Isothiocyanates.[a]

entry	R	time, h	yield, %[b]
1	cyclohexyl	2.5	99(85)
2	Me	3.5	94
3	n-Bu	3	92(73)
4	t-Bu	3	81(69)
5	$PhCH_2$	3.5	96(79)

a) Isocyanide (2.5 mmol), sulfur (3 mmol), tellurium (0.02 mol%), triethylamine (6 mmol), THF (5 mL), reflux.
b) Glc yield (isolated yield).

The tellurium catalyzed formation of isothiocyanates **1** may be expressed by the catalytic cycle shown in Scheme 1, by analogy of selenium catalysis. The reaction of isocyanides with tellurium may form isotellurocyanates **2** as an intermediate, though several attempts to confirm **2** failed.[8] Thus transiently formed isotellurocyanates **2** immediately react with sulfur to give isothiocyanates **1** by Te-S exchange. This is marked contrast to the selenium catalysis where the reaction of isoselenocyanates with sulfur is rate determining. Accordingly, it is suggested that marvelous catalytic activity of elemental tellurium might be due to the high reactivity of isotellurocyanates **2**.



Scheme 1. Te catalyzed formation of isothiocyanates.

Acknowledgement

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2 The direct reaction of aromatic isocyanides with sulfur was reported to be very sluggish,[3] and moreover aliphatic isocyanides hardly react with sulfur.[4] In general, isothiocyanates have been prepared by thermal decomposition of dithiocarbamates produced by the reaction of amines with carbon disulfide.[5]

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7 Reaction conditions: cyclohexyl isocyanide (2.5 mmol), sulfur (3 mmol), tellurium or selenium catalyst (0.5 mol%), triethylamine (6 mmol), THF (5 mL), 50°C.

8 Organic isotellurocyanates have not been prepared so far. Several attempts for their synthesis by the reaction of isocyanides or organocyanosilanes with tellurium and by photoinduced isomerization of organic tellurocyanates failed, see: ref 1b, pp585.

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