

# Isonitriles in Fischer–Tropsch catalysis

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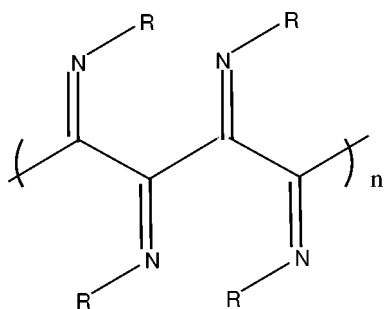
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The growth of saturated carbon–carbon chains has been detected in the reaction of isonitriles with Raney nickel and Raney cobalt in liquid ammonia and under hydrogen pressure. The plausible mechanism for this Fischer–Tropsch-like reaction with isonitrile instead of carbon monoxide is discussed.

**Keywords:** isonitrile, Raney, nickel, cobalt, hydrogen, saturated, carbon–carbon bond

## 1. Introduction

Isonitriles,  $R-N\equiv C:$ , as a class of organic compounds with an unsaturated functional group could be polymerized into the high molecular weight products [1]. A variety of nickel salts has been shown to act as very efficient catalysts for polymerization of aliphatic and aromatic isonitriles, including monomers with additional double or triple bonds, with metal ligating functions, with crown ether rings, with donor–acceptor groups, and with stable radical substituents [2]. The structure of the isonitrile polymer consists of unsaturated  $C=N$  double bonds as the monomeric units:



Some of the polymers based on isonitriles can be resolved into left-handed and right-handed helices which do not racemize even at elevated temperatures [3].

The isonitrile function could be reduced to N-monomethylamines by commonly used reducing agents such as  $LiAlH_4$  [4]. The nickel metal [5] or the nickel cluster  $Ni_4[CNMe_3]_7$  [6] are effective catalysts for the hydrogenation of the isonitriles in the mixture of N-monomethylamines and corresponding primary amines, but no polymerization of isonitriles has been reported although the polymerization should be expected on the basis of the literature results shown above. The solutions of metals (lithium, sodium, potassium, and calcium) in liquid ammonia reduc-

tively cleaves isonitriles to their corresponding hydrocarbons [7,8].

A two-step mechanism has been postulated in which the addition of the first electron leads to formation of an anion-radical intermediate which can accept a second electron leading to the formation of a carbanion intermediate and cyanide ions [9]. Again, no polymerization products have been detected.

In this communication, we report the formation of a saturated carbon–carbon bond and the chain growth in the reaction of the isonitriles with Raney nickel and Raney cobalt under hydrogen pressure in liquid ammonia.

## 2. Experimental

The catalytic reactions were performed in a 50 ml stainless-steel reactor equipped with a stirrer (Autoclave Engineers). All assembling and charging procedures were carried out in a glove box in nitrogen atmosphere. The autoclave was flushed with hydrogen, liquid ammonia (35 ml) was pumped into the autoclave by an ISCO pump and heated to 80 °C before subjecting the reaction mixture to 1000 psi of hydrogen pressure (total pressure). The rotation was 1500 rpm. In the typical reaction procedure 5.0 g of Raney nickel or Raney cobalt were charged together with 2.5 g of an isonitrile; 35 ml of liquid ammonia were pumped into the autoclave. It was heated to 80 °C and the pressure was adjusted to 1000 psi with hydrogen. After 3 h the reaction mixture was cooled off to ambient temperature and filtered from the catalyst by means of the filter incorporated in the autoclave. The filtrate was analyzed by GC/MS with chemical ionization and electron impact (Varian 3800GC, Saturn 2000 MS and HP 5890 GC).

The samples of the isonitriles (*n*-butyl, isopropyl, *tert*-butyl, benzyl and *tert*-octylisonitriles) were purchased from Aldrich and Strem and used without further purification.

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above. There is not enough information to assign the exact structures. We also observed low-intensity ( $<0.5\%$ ) GC lines in the region where high-boiling compounds would be expected. We did not attempt to shift the reaction into the formation of the heavier or lighter condensation products by varying temperatures, ratio or by scouting the different catalysts. The N-monomethylbutylamine was the major component in the reaction mixture, the butylamine and N,N'-dibutylethylenediamine were present in about equal amounts at 20% of the intensity of N-monomethylbutylamine; the rest of the products are about 1% of the intensity of the N-monomethylbutylamine.

The redistribution of the products in the reaction of isopropyl isonitrile with Raney nickel was different. The product with the single saturated carbon-carbon bond, in this case N,N'-diisopropylethylenediamine, was the major component in the reaction mixture (scheme 2).

It was also not as selective a reaction, several high-boiling products were recorded by GC/FID with small intensities. The structures of the above products were confirmed by matching them with known mass spectra from the library.

$$\text{Bu}-\text{N}^+\equiv\text{C}^- \xrightarrow[\text{+ H}_2, 1000 \text{ psi}]{\text{Ra-Co, NH}_3} \begin{array}{c} \text{H} \\ | \\ \text{H}-\text{N} \\ | \\ \text{Bu} \end{array} + \begin{array}{c} \text{CH}_3 \\ | \\ \text{H}-\text{N} \\ | \\ \text{Bu} \end{array} + \begin{array}{c} \text{CH}_2\text{-CH}_3 \\ | \\ \text{H}-\text{N} \\ | \\ \text{Bu} \end{array} +$$

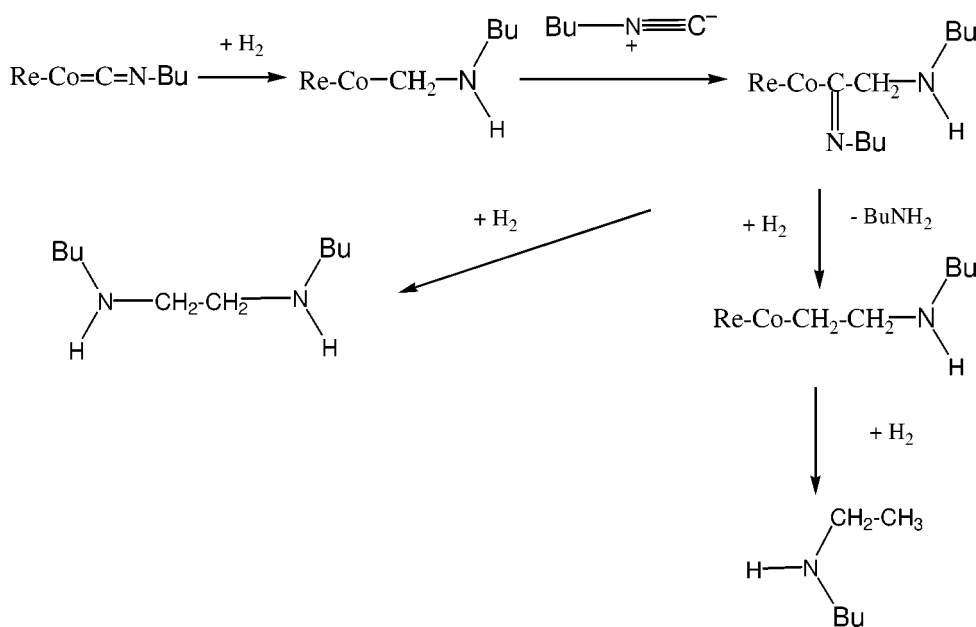
$$\begin{array}{c} \text{CH}_2\text{-CH}_2\text{-CH}_3 \\ | \\ \text{H}-\text{N} \\ | \\ \text{Bu} \end{array} + \begin{array}{c} \text{Bu} \\ | \\ \text{H}-\text{N}-\text{CH}_2\text{-CH}_2-\text{N}-\text{H} \\ | \qquad \qquad | \\ \text{Bu} \qquad \qquad \text{H} \end{array} + \begin{array}{c} \text{Bu} \\ | \\ \text{H}-\text{N}-(\text{CH}_2)_3-\text{N}-\text{H} \\ | \qquad \qquad | \\ \text{Bu} \end{array}$$

$$+ \begin{array}{c} \text{Bu} \qquad \qquad \text{Bu} \\ | \qquad \qquad | \\ \text{H}-\text{N}-(\text{CH}_2)_4-\text{N}-\text{H} \\ | \qquad \qquad | \\ \text{H} \end{array} \quad *$$

\* - structural isomers are possible

Scheme 1.





Scheme 3.

The plausible mechanism of the formation of the saturated carbon–carbon bond from isonitriles could be the same as with the Fischer–Tropsch reaction mechanism for carbon monoxide. An isonitrile could coordinate with nickel or cobalt on the surface of Raney metals. After the initial hydrogenation of the double carbon–nitrogen bond, the insertion of the second molecule of isonitrile into the metal–carbon bond will lead to the creation of the carbon–carbon bond and, subsequently, carbon chain. The branching could occur by other possibilities, but we do not have sufficient data to speculate on it at this point of the research. The primary amines, like butylamine or isopropylamine in the above reactions, would be by-products in the carbon–carbon chain growth reaction. Water is the analogous product in the Fischer–Tropsch reaction.

The ability of isonitriles to insert into metal–carbon bonds (where metals are comprising from Raney metals) are well documented [10,11]. The intriguing reductive coupling of carbon monoxide with methyl isonitrile was reported [12]. The formation of the unsaturated carbon–carbon bond between bridging isonitriles is also known [13–16]. The presence of the hydrogen in our systems and the ability of Raney nickel and cobalt, not only to hydrogenate but also to oligomerize the isonitriles, made it possible to see the formation of saturated carbon–carbon bonds.

#### 4. Conclusion

Isonitriles, as isoelectronic analogs of carbon monoxide, undergo similar Fischer–Tropsch reactions with the formation of the saturated carbon–carbon bonds in amines or diamines.

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