Journal of Molecular Catalysis, 75 (1992) 209–218
M2960

Hydrodecyanation*

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(Received December 9, 1991; revised March 5, 1992)

Abstract

Nitriles such as benzonitrile and acetonitrile react with hydrogen in the presence of a variety of catalysts to form HCN and hydrocarbons. The preferred catalyst to convert benzonitrile to benzene and HCN is 1% Pd/SiO_2. The selectivity is essentially 100% at 30% conversion at 725 K. The major side-reaction with inferior catalysts is hydrogenolysis to toluene and ammonia. HCN yields increase with non-acidic supports and higher operating temperature.

Introduction

Most studies of the vapor phase hydrogenolysis of substituted aromatics involve the conversion of toluene to benzene and methane. This reaction is an industrially important source of benzene [1]. Toluene hydrogenolysis proceeds both thermally and catalytically. The catalytic reaction occurs at lower temperatures and produces fewer byproducts. Radical generators enhance the reaction [2].

$$In^{\bullet} + PhX \longrightarrow InX + Ph^{\bullet}$$

$$Ph^{\bullet} + H_2 \longrightarrow PhH + H^{\bullet}$$

$$H^{\bullet} + PhX \longrightarrow HX + Ph^{\bullet}$$

$$\text{net:}\quad PhX + H_2 \longrightarrow PhH + HX$$

X = Me, Cl, OH, CN

Hydrogenolysis of chlorobenzenes [3], anilines [4], phenols [5] and benzonitriles [6] have also been reported. The reactions are important both as synthetic methods and as a means of removing heteroatoms in petroleum refining.

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*Contribution No. 5066.

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0304-5102/92/$5.00

Specifically for the case X = CN, two different inventors have patented the thermal equilibration,

$PhH + HCN = PhCN + H_2$

one from either direction [7a, b]. Cyanonaphthalenes pyrolyze at 1100 K to dicyanonaphthalenes and naphthalene. Isomerization of the cyanonaphthalene occurs simultaneously [7c]. Although most hydrogenolysis studies have involved aromatic compounds, there is no mechanistic reason to exclude aliphatic compounds. Acetonitrile thermally hydrodecyanates to methane and HCN in excellent yield [8].

The catalytic *liquid-phase* hydrogenation of nitriles, such as benzonitrile, with Group VIII metal catalysts is a well-documented reaction. The usual products are benzylamine and its condensation products [9].

Hata studied the catalytic *vapor-phase* hydrogenolysis of benzonitrile with nickel catalysts and observed two paths [10]. At 520 K the sole products were toluene and ammonia, presumably by hydrogenolysis of a benzylamine intermediate. Andrade *et al.* [11] reinvestigated this reaction, and showed that the CN group could be used to protect CH_3 in a synthetically useful manner.

At 620 K Hata [10] obtained a significant yield of carbon–carbon hydrogenolysis to benzene and methylamine. Dehydrogenation of methylamine to HCN is thermodynamically possible only above this temperature [12]. Many years later other workers found catalysts which produced HCN from methylamines in good yields [13]. There are homogeneous models for possible elemental steps in hydrodecyanation. Benzonitrile oxidatively adds to low-valent transition metal complexes [14(a)]; the reverse reaction, reductive elimination, also occurs [14(b)].

We were interested in catalysts to convert benzonitrile and hydrogen to HCN and benzene [15]. This reaction would provide a route to HCN not requiring natural gas as a carbon source. Even though toluene is much more expensive than methane, a mole of benzene is worth more than a mole of toluene. Thus the methyl group of toluene has a *negative* raw material cost, and that is a nice starting point for a new process.

Our goal was to discover catalysts and substrates which undergo the hydrodecyanation reaction. We also present our studies of the side reactions which limit the reaction's utility. It is beyond the scope of this work to study all catalysts with all substrates under all conditions of partial pressure, contact time and temperature. In this work we merely seek a broad outline of this new catalytic reaction.

Results

Thermodynamics

Table 1 gives the free energies and enthalpies for some of the reactions of interest in hydrodecyanation systems [12]. Benzonitrile hydrodecyanation,

TABLE 1

Thermodynamics of some hydrodecyanation reactions

	Reaction	$\Delta G(300)$	$\Delta G(900)$	$\Delta H(600)$[a]
			(kcal/mol)	
1	$PhCN+H_2 \rightarrow HCN+PhH$	−2.6	−3.8	−2.5
2	$MeCN+H_2 \rightarrow HCN+CH_4$	−8.7	−9.7	−13.3
3	$PhCN+3H_2 \rightarrow PhCH_3+NH_3$	−36.9	−4.2	−54.4
4	$PhCH_3+H_2 \rightarrow CH_4+PhH$	−10.3	−9.4	−11.2
5	$2HCN+2H_2 \rightarrow CH_3CN+NH_3$	−35.9	−0.1	−54.8
6	$CH_3NH_2 \rightarrow HCN+2H_2$	+20.9	−13.8	+39.2

[a] Temperatures in K.

TABLE 2

Thermal hydrodecyanation of benzonitrile

Temperature (K)	Contact time (s)	Mole ratio (H_2/PhCN)	% Conversion PhCN to HCN
825	8	1	0.3
875	8	1	1
925	16	2	7

eqn. (1) in Table 1, is always favorable from both points of view. The equilibrium constant is small, so the reverse reaction is significant and conversion is thermodynamically limited. At 825 K the equilibrium constant allows only 70% conversion of benzonitrile to HCN with a benzonitrile/ hydrogen ratio of unity. This near-zero free energy difference explains how two different investigators could observe the reaction from opposite directions [7].

Hydrodecyanation of acetonitrile, eqn. (2) in Table 1, is particularly favorable because methane is so stable. Because hydrogenolysis of the nitrile group to ammonia, eqn. (3) in Table 1, involves a volume contraction, this reaction becomes less favorable at higher temperatures. The equilibrium constant is less than one above 975 K. The demethylation of toluene to benzene, eqn. (4), is more favorable than the decyanation of benzonitrile, eqn. (1), at all temperatures. Condensation of two nitriles with the elimination of ammonia, eqn. (5), is very favorable at low temperatures. Dehydrogenation of methylamine to HCN, eqn. (6), is only favorable at high temperatures.

Thermal reaction

Benzonitrile and hydrogen give HCN and benzene in the absence of catalyst above 900 K (Table 2). The gas phase shows no other low molecular weight products. However, cold spots in the reactor become coated with a brown tar and higher pyrolysis temperatures give more tar. The thermal hydrodecyanation of benzonitrile is considerably slower than that of acetonitrile and is not a practical reaction. The thermal reaction *is* a non-negligible background for any catalytic studies of benzonitrile hydrodecyanation.

Catalyst effects

The most obvious way to modify Hata's conditions to make HCN would be to raise the temperature to the point where the thermodynamics favor HCN from methylamine. However, Hata's nickel catalysts totally destroy the organic feed under these conditions. The products are hydrogen and nitrogen in the vapor phase and a massive carbon deposit on the catalyst. Other first-row metals, both supported and unsupported, behave similarly.

Table 3 shows representative hydrodecyanation catalysts and their efficiency in benzonitrile hydrodecyanation. We grade catalyst performance by the ratio of HCN produced with the catalyst candidate compared to that produced in the thermal reaction under otherwise identical conditions. Our definitions focus on HCN formation, especially the fate of the nitrogen. Usually the major nitrogen-containing byproduct is ammonia from the hydrogenolysis of benzonitrile to toluene. We seldom see much nitrogen.

$$\text{PhCN conversion} = \frac{100 \times (\text{PhCN} - \text{PhCN}_0)}{(\text{PhCN} + 2\text{N}_2 + \text{NH}_3 + \text{HCN} + \text{CH}_3\text{CN})}$$

TABLE 3

Hydrodecyanation catalysts

Catalyst	Temp. (K)	PhCN Conversion	HCN Selectivity	$\frac{\text{HCN}}{\text{Blank}}$
Pt gauze	925	0	0	0
Cr_2O_3	925	12	77	1.3
MnO	925	27	18	0.7
MgO	925	23	84	4
Al_2O_3	825	23	15	12
1% Cr_2O_3/SiO_2	825	13	58	25
10% $Cr_2O_3Al_2O_3$	825	39	17	22
0.5% Ru/Al_2O_3	825	40	40	53
0.5% Pd/Al_2O_3	875	48	48	25
0.5% Pt/Al_2O_3	825	85	11	30
0.5% Rh/Al_2O_3	825	54	27	50
1.0% Pd/Si-Al	825	35	12	15
1.0% Pd/C	825	16	69	35
1.0% Pd/ZnO	875	5	75	4
1.0% Pd/MgO	825	33	79	85
1.0% Pd/SiO_2	825	55	75	**140**
1.0% Pt/SiO_2	825	8	100	25
0.4% Ru/SiO_2	825	11	91	35
0.5% Rh/SiO_2	825	38	15	20
5.0% Ir/SiO_2	825	47	13	20

HCN selectivity = HCN/(HCN + $2N_2$ + NH_3 + CH_3CN)

HCN formation = HCN selectivity × PhCN conversion

Bulk metals such as Pt gauze are not effective catalysts, presumably because of their low surface area. This is the commercial catalyst used to prepare HCN by methane ammoxidation. Oxides such as alumina and magnesia can produce as much as ten times more HCN than a blank at 925 K. Low HCN productivity can arise from deficiencies in either activity or selectivity. At lower temperature, oxide catalysts lose both their selectivity and activity. Supported second- and third-row Group VIII metal catalysts are also hydrodecyanation catalysts. At the higher temperatures these more expensive catalysts show no advantages over the cheaper oxides. At lower temperatures, supported metals maintain both activity and selectivity to a higher degree.

Many materials such as supported first-row Group VIII metals are quite active for benzonitrile destruction. They are not selective for HCN formation. Palladium is the most selective metal. Neutral or basic supports such as silica or magnesia are superior to more acidic supports such as alumina or silica–alumina. Platinum and ruthenium are selective, but not very active; rhodium and iridium are active, but not very selective. We studied the reaction with 1% Pd/SiO_2 in more detail.

Kinetics

Conversion passes through a maximum at 825 K with 1% Pd/SiO_2 and constant contact time, as shown in Table 4. Selectivity is 100% at low temperature and remains reasonably high as temperature increases. Selectivity decreases as conversion increases in this temperature range. The rate maximum may reflect a balance between rising intrinsic surface rates and decreasing PhCN or hydrogen adsorption.

There is essentially no parallel hydrogenolysis to toluene and ammonia with this catalyst. Yield losses at higher conversions are entirely due to consecutive processes which destroy the initially formed HCN.

TABLE 4

Effect of temperature on hydrodecyanation of benzonitrile with 1% Pd/SiO_2

Temperature (K)	Conversion of PhCN	Selectivity to HCN
675	12	84
725	21	100
775	31	94
825	53	85
875	45	90
925	40	92

Selectivity

Each catalyst has its own characteristic HCN/ammonia product ratio. This selectivity is insensitive to either temperature or conversion. The first observation suggests that the two processes have similar activation energies. The second suggests that the two products come from parallel rather than sequential processes. HCN selectivity for a given metal is always better with a SiO_2 support than with Al_2O_3. Selectivity is a function of the ratio of the starting materials, with more hydrogen favoring ammonia formation.

We determined the relative rates of hydrodecyanation and hydrodealkylation by passing hydrogen and *p*-toluonitrile over 1% Pd/SiO_2. At low conversions the ratio of HCN to methane formed is ~50. We obtained a similar result from an equimolar mixture of benzonitrile and toluene. Hydrodecyanation is faster than hydrodealkylation with this catalyst, despite the more favorable free energy change for hydrodealkylation.

$$PhCN + CH_4 \longleftarrow MeC_6H_4CN + H_2 \longrightarrow PhMe + HCN$$

We observed some acetonitrile in almost every benzonitrile hydrodecyanation, from mere traces to several percent. Given that acetonitrile hdyrodecyanates readily to methane and HCN, its presence was somewhat mysterious.

Other substrates

We studied the hydrodecyanation of other nitriles with a Cr_2O_3/Al_2O_3 catalyst, being interested in how well the catalyst performs with each substrate. Table 5 gives the conditions used and the ratio of HCN produced in the presence of a catalyst to that produced with an equal volume of SiC. The contact time was adjusted to produce very low conversions, so this ratio could adequately characterize catalyst performance.

The catalyst is very efficient with $PhCH_2CN$, PHCH=CHCN and $NCCH_2CN$, producing more than 100 times as much HCN as the control. Benzyl cyanide

TABLE 5

Hydrodecyanation of nitriles with 19% Cr_2O_3/Al_2O_3[a]

Nitrile	RCN (ml/h)	H_2 (ml/min)	$\frac{HCN}{Blank}$
$PhCH_2CN$	2	40	110
MeCN	2	36	21
Me_3CCH_2CN	2	15	3.2
PhCH=CHCN	5	18	>110
$CH_2=C(Me)CN$	2	18	2.8
$CH_2=CHCN$	2	18	16
$NCCH_2CN$	[b]	20	180
$2\text{-}MeC_6H_4CN$	5	40	4.3
2-cyanopyridine	[b]	20	7.4

[a] 875 K, catalyst weight 2–5 g.

[b] Gaseous hydrogen was passed over molten substrate 10–20 K below its boiling point.

reacts with hydrogen to give HCN and toluene and none of the alternative hydrogenolysis products acetonitrile and benzene. Acetonitrile forms HCN and methane thermally, and the reaction also responds well to catalysis. Acetonitrile hydrodecyanation also produces trace amounts of propionitrile. The catalyst is less effective with sterically hindered nitriles such as methacrylonitrile and *o*-toluonitrile.

Aliphatic nitriles such as propionitrile, t-butyl cyanide and cyanocyclohexane give HCN, but the mechanism is dehydrocyanation rather than hydrodecyanation. The reaction produces HCN and alkenes in the absence of added hydrogen. Hydrogen sequentially reduces the alkenes to alkanes.

Neopentyl cyanide hydrodecyanates, but the catalytic enhancement is not large. Acrylonitrile hydrodecyanates, but the mechanism is probably addition–elimination, as large amounts of propionitrile accumulate at intermediate conversion.

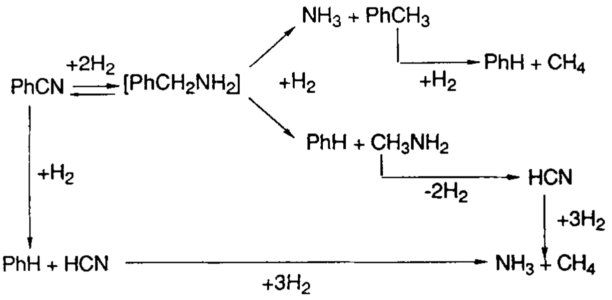
Discussion

We will discuss the effect of catalyst variables using benzonitrile as substrate and the effect of reaction variables using Pd/SiO_2 as catalyst. Scheme 1 shows the reaction network which forms the framework for this discussion.

Benzonitrile reacts with hydrogen in parallel and sequential paths to give products from hydrogenolysis of either carbon–carbon or carbon–nitrogen bonds. Nickel catalysts first hydrogenate the cyano group. In the liquid phase the reaction stops at the amine stage, with no single-bond cleavage. In Hata's vapor-phase work, the next step is carbon–carbon bond cleavage to give benzene and methylamine.

In this higher temperature, vapor-phase study using second- and third-row supported metals or first-row metal oxides, it does not appear to be necessary to invoke hydrogenation products as intermediates to HCN. Cleavage of the C–CN bond and the C–N bond are parallel reactions leading to product and byproducts respectively. In addition, sequential reactions of HCN lead to other byproducts.

The major variables which affect this partitioning are the acidity of the catalyst and the reaction temperature. More acidic catalysts and lower



Scheme 1.

temperatures favor cleavage of the carbon–nitrogen bond to give toluene and ammonia.

In the nitrile hydrogenolysis path the potential intermediates, benzaldehyde imine and benzylamine, are more basic than their precursors. Each should remain bound to an acidic catalyst until only the thermodynamically favored product, ammonia, desorbs. A neutral or basic support might minimize this pathway by promoting early product desorption.

$$\mathrm{PhCN} \longrightarrow \mathrm{PhCH{=}NH} \longrightarrow \mathrm{PhCH_2NH_2} \longrightarrow \mathrm{PhMe} + \mathrm{NH_3}$$

The temperature effect may have its origins in thermodynamics. The free energy change of benzonitrile and hydrogen to HCN and benzene is favorable at all temperatures. In contrast, the hydrogenolysis to toluene and ammonia is more favorable at low temperatures because of the volume contraction involved. Thus we would expect that the selectivity to HCN would increase with temperature. Solid acids can catalyze benzonitrile formation from toluene and ammonia above 900 K [16].

Palladium as the preferred metal seems to correlate with its poor performance as a nitrile hydrogenation catalyst in liquid phase reactions [17]. Its utility lies less in its activity for benzonitrile conversion than its selectivity to HCN. First-row elements are extremely active benzonitrile hydrogenation catalysts, but give no HCN under our conditions.

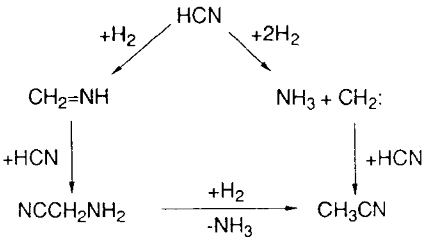
Sequential methane formation by hydrogenolysis of HCN is not a significant reaction with $\mathrm{Pd/SiO_2}$. The ratio of the rate of HCN formation from benzonitrile to its hydrogenolysis to methane and ammonia with this catalyst is approximately ten, independent of temperature. This sequential reaction accounts for the decreasing selectivity to HCN at increasing conversion in Table 4.

$$\mathrm{PhCN} \longrightarrow \mathrm{HCN} \longrightarrow \mathrm{CH_4} + \mathrm{NH_3}$$

Acetonitrile is a surprising byproduct from benzonitrile and hydrogen, since it also efficiently hydrodecyanates. Thermodynamics does not allow its synthesis from methane and HCN. Hydrogenolysis of benzyl cyanide, a rather unlikely intermediate to be sure, does not give acetonitrile. We would expect, though we have not shown, that in a mixture of PhCN and $\mathrm{CH_3CN}$, the PhCN would be more strongly adsorbed, and therefore would preferentially hydrodecyanate.

The Olivés [18] described a potential mechanism for nitrile homologation. formaldehyde imine might be a surface intermediate in the hydrogenolysis of HCN to methane and ammonia. We consider two possible paths to convert this intermediate to acetonitrile. They differ only in the order in which HCN and H_2 react.

One path begins by addition of HCN to form surface aminocyanomethane. The other begins by α-hydrogenation to ammonia and a bound methylene. Neither mechanism is unique to HCN or formaldehyde imine. Both mechanisms allow the analogous transformation of acetonitrile, via acetaldehyde imine, to propionitrile, which we have also observed.



This nitrile homologation is the nitrogen analog of the Fischer–Tropsch reaction.

We cannot comment on whether the active site involves more than one catalyst atom. Kaesz's nitrile hydrogenations on iron clusters [19] may be a good model for the heterogeneous nitrile hydrogenolysis side reaction. The actual mechanism may involve alternate oxidative addition and reductive elimination cycles, involving metal- or oxide-centered hydrides and cyanides.

Experimental

All hydrocarbons and gases were obtained from commercial sources and used without additional purification. The experimental apparatus and methods of control have been previously described [20]. All temperatures are in K.

An HP 5700 GC with a thermal conductivity detector performed on-line GC analyses. We used a 4 ft × 1/4 in ss column of Porapak Q® and a carrier gas flow of 20 ml/min. The temperature program was 398 K for 2 min to elute the fixed gases and then +32 K/min to 523 K to elute benzonitrile.

We obtained most of our catalysts from commercial sources. We prepared the preferred 1% Pd/SiO_2 by co-evaporating palladium nitrate and Ludox® silica sol to dryness and calcining overnight at 800 K. Coked catalysts could be repeatedly regenerated by heating in air.

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